THE INTERACTION OF CHARCOAL WITH AQUEOUS SOLUTIONS OF STRONG INORGANIC ACIDS AND BASES

by

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INTRODUCTION

In general, gases are reversibly adsorbed by charcoal, so that either evacuation or increase in temperature causes complete desorption of unchanged gas. This holds for oxygen at very low temperatures, as was demonstrated by Dewar,[i] but at normal room-temperatures, and above, the adsorption is wholly irreversible. As early as 1863 R. Angus Smith[ii] reported that oxygen as such was not recoverable from charcoal, carbon dioxide being formed when the charcoal was heated, even at temperatures below 100°. It has been shown by Baker[iii] and others[iv,v,vi,vii] that actually both carbon dioxide and carbon monoxide are evolved.

Rhead and Wheeler[iv] suggested that the irreversibly adsorbed or "fixed" oxygen formed a physico-chemical "complex" with the surface atoms of the charcoal. Since the complex gave rise to carbon dioxide and carbon monoxide in proportions which varied with the temperature at which the oxygen was originally "fixed", it was considered to be of variable composition and hence was formulated as C_xO_y. Most workers in this field[v,vii] have adopted essentially the same point of view, the oxygen being described by some as "chemisorbed" on the charcoal, and by others as forming "surface oxides" with it. In brief, the oxygen is regarded as linked by bonds, co-valent in type, to surface

atoms of carbon which remain held in the lattice structure of the solid material.

Very high temperatures are required to remove chemisorbed oxygen and Langmuir[viii] has reported that, after treatment with oxygen, a carbon filament continues to evolve traces of oxides at 2000°. Very large heats of sorption have also been reported for oxygen. Keyes and Marshall[ix] obtained a heat of 70,000 cal. per mole of oxygen sorbed at 0°, and Garner and co-workers[x] report heats of 60,000-70,000 cal. per mole at room-temperatures. Moreover, it would appear from Garner's work that the heat of sorption increases very considerably with rise in temperature, although recently Weller and Young[xi] have reported a heat of 65,000 cal. per mole of oxygen sorbed at 400°. These large heats of sorption indicate clearly that the fixed oxygen is held at the surface of carbon by very strong bonds.

The behaviour of charcoal in the adsorption of inorganic acids and bases from aqueous solution has been considered by some workers to indicate the existence of at least two types of surface oxide. Bartell and Miller[xii] observed that charcoal which had been heated at 1000° would adsorb acids but not bases.[1] However, in 1929 Kruyt and de Kadt[xiii] reported that while sodium hydroxide was not

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[1] In a later paper (J. Phys. Chem., 1932, 36, 2967), Miller reports that negative adsorption of sodium and potassium hydroxides occurs when the charcoal has been heated at 1000°.

adsorbed by charcoal heated at 1000° in vacuo or in carbon dioxide, considerable adsorption occurred when the charcoal was heated at 400° in a stream of oxygen. Schilov and co-workers[xiv] found that sugar charcoal adsorbed both acid and alkali, in proportions depending upon the temperature at which the charcoal was heated in air. Maximum adsorption of sodium hydroxide and minimum adsorption of hydrochloric acid occurred with charcoal treated with air at 500°. Treatment at 250° or 1000° gave charcoal which adsorbed acid but not base. Schilov concluded that an "acidic" oxide(C) was formed in varying amounts over a wide range of temperatures (300°-800°), but that 500° was the most favourable temperature for its formation. He postulated that the acidic oxide was formed by oxidation of a "basic" oxide(B), and that above 850° the latter alone existed. The sorption of acid and alkali was attributed to interaction with the appropriate oxide. Subsequent investigations by Kolthoff,[xv] Miller[xvi] and King[xvii] yielded, broadly speaking, similar results and conclusions. The careful and extensive work of King, however, showed that there was maximum adsorption of sodium hydroxide and no adsorption of hydrochloric acid by sugar charcoal treated with moist oxygen at 400° (cf. Schilov's optimum temperature of 500°).

As a result of an investigation of the adsorption by charcoal of a number of organic compounds,

Ockrent[xviii] was led to question the presence of any fixed oxygen on the surface of charcoal. He carried out a series of experiments in which sugar charcoal was heated in a stream of purified nitrogen with step-wise increase in temperature to 950°, and recorded that water was evolved in stages (or "rushes") corresponding to definite temperatures.[xix] The amounts of water evolved were determined, as also were the amounts of carbon dioxide (including converted carbon monoxide) and water obtained by combustion of the charcoal after the treatment with nitrogen. It appeared that the initial weight of the charcoal was equal simply to the sum of the weights of carbon and water present. Ockrent, therefore, in contrast with the general view, denied the existence of fixed oxygen, and suggested that the behaviour of charcoal towards inorganic acids and bases depended on the extent to which its surface was covered with high-temperature adsorbed water. He considered that alkali is adsorbed by a charcoal surface on which such water is present, while acid is adsorbed by a surface freed from water.

In support of his contentions, Ockrent refers to the observation of Kolthoff that while the amount of sodium hydroxide adsorbed by charcoal treated with oxygen at 400° was unaffected by subsequent heating in vacuo for 30 hours at 500°, a marked decrease in alkali-adsorption was produced by heating for 24 hours at 575°. Ockrent points out that in

his experiments, relatively little water was evolved when the temperature was raised from 250° to 500°,[1] but a large amount was liberated when the temperature was raised to, and above, 575°. However, the matter is complicated by the results of King, who found that the alkali adsorbed per unit area of surface of charcoal treated with oxygen at 480°, was only one-third of that observed when the treatment was carried out at 380°. This would indicate that a change in the state of the charcoal surface occurs well below 575°.

Ockrent lays great stress on reports that the presence of moisture in the air or oxygen with which charcoal is treated, promotes the adsorption of alkali. Miller[xvi] states: "for rapid formation of the complex acid it is necessary to heat the charcoal at 300°-400° in the presence of air and water vapour, although action takes place slowly at room temperature." Kolthoff presents data which appear to support his statement that "water vapour seems to promote the formation of the acid substance". King consistently used moist oxygen in the treatment of his charcoal. It should be noted also that Kruyt and de Kadt do not specify the state of their oxygen and Schilov appears to have used undried air. In all cases oxygen was present and no one seems to have examined the effect of heating in water vapour

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[1] Heating up to 250° caused the loosely held water, adsorbed at room temperature, to be liberated.

alone.

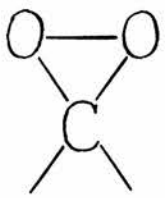
Kolthoff found that considerable quantities of alkali were adsorbed by sugar charcoal heated to 950° and then treated with dried oxygen at 400°. This might seem sufficient to disprove Ockrent's hypothesis, but it must not be overlooked that occluded water would not be removed at 950° and might be present on the fresh charcoal surface produced by the subsequent treatment with oxygen at 400°. Moreover, sugar charcoal may contain hydrogen as such or in the form of various groupings,[xx,xxi] and Riley[xxii] has drawn attention to the influence of this hydrogen on the properties of charcoal. It is therefore possible that water is formed from such hydrogen during treatment with dried oxygen. In addition it should be noted that Kolthoff did not outgas the charcoal, and does not specify his method of drying the oxygen.

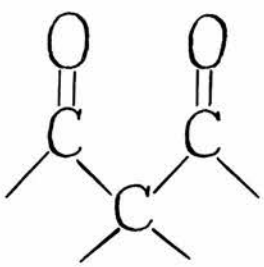
Kolthoff observed that when charcoal was treated with moist oxygen, the rate of combustion was greater than when dried oxygen was used. It seems possible, therefore, that the favourable influence of water vapour on the adsorption of alkali was due to the provision of a larger specific surface area, as the result of increased combustion.

Although chemisorption of oxygen by charcoal must be regarded as an established fact, it will be apparent from the foregoing that the role of adsorbed water in relation to the interaction of

charcoal with inorganic acids and bases has remained obscure. In the present investigation, therefore, the author has in the first place carried out experiments designed to test the various arguments put forward by Ockrent in support of his theory. The results have shown the theory to be fallacious and that the adsorption of alkali, at least, must be connected with the chemisorption of oxygen. Attention was consequently then turned to the nature of the relationship between the two phenomena and, therefore, to the manner in which the oxygen concerned is held by the carbon surface.

Originally Rhead and Wheeler stated merely that a loose physico-chemical complex was formed, with no definite ratio of oxygen to carbon atoms, but various more precise suggestions as to the mode of binding of the oxygen have since been made. Langmuir suggested that the oxygen was dissociated and the atoms held by double bonds to individual carbon atoms. Garner agreed that the oxygen evolved as carbon monoxide would probably be held in this way but added that the oxygen liberated as carbon dioxide would probably be held by a carbon atom in the undissociated form. The linkages pictured are shown below:





Schilov assumed the existence of three different oxides A, B and C, the first two (A and B) being basic, and the third (C) acidic.[1] In contrast, Strickland-Constable[vii] has postulated the existence of a "vast variety of oxides", and has maintained that only a small fraction of the total chemisorbed oxygen had acidic and basic properties.[xxiii] Recently Villars[xxiv] has published evidence for the presence of hydroxyl (-OH) and carbonyl (=C=O) groups on the surface of charcoal. He concludes that the oxygen linked in these ways amounts to only about 26% of the total, and he assumes that the remainder ("unreactive" oxygen) is held by etheric linkages (-C-O-C-). However, the oxygen content of the charcoals examined by Villars was very small and, moreover, the hydroxyl oxygen may well have been that of water.[2] Clearly, further information is necessary for the elucidation of the state (or states) and properties of fixed oxygen.

For convenience, the following account of the author's work is presented in two parts. Part I comprises those sections of the investigation concerned specifically with Ockrent's theory of the role of water in the adsorption of acids and bases by charcoal. Part II deals with experiments, of

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[1] Oxide A would not be present normally since it was supposed to change rapidly into B at oxygen pressures above 2 mm.

[2] The highest drying temperature employed was only 140°.

importance in connection with Ockrent's theory, but designed primarily to obtain information with regard to the role of fixed oxygen in the adsorption.

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xiii Kruyt and de Kadt, Kolloid-Z., 1929, 47, 44.

xiv Schilov et al., Z. physik. Chem., 1930, 149, 211.

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xvii King, J.C.S., 1937, 1489.

xviii Ockrent, J.C.S., 1932, 1864.

xix Ockrent, J.C.S., 1932, 291.

xx Beilby, J. Soc. Chem. Ind., 1922, 41, 342T.

xxi Lowry, J.A.C.S., 1924, 56, 824.

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PART I - THE ROLE of ABSORBED WATER

EXPERIMENTAL

Preparation of Sugar Charcoal[1]

Charcoal was prepared from Griffin and Tatlock's A.R. Sucrose by heating small quantities at a time in pyrex glass basins (9 cm.) with bunsen burners. The basins were placed on wire gauze and two large clock glasses were clamped about a foot above them to act as a protection against the entrance of atmospheric dust. When the sugar had been converted into a thick black tar by heating with a moderate flame, it was ignited and allowed to burn out, and as the flames began to die down the basins were heated with a full bunsen flame in order to drive off as much as possible of the volatile matter. The first lot of charcoal from each basin was rejected and thereafter only the light, flaky charcoal which could be easily removed from the basins was collected. This crude charcoal was broken up into smaller pieces by crushing it in a large porcelain basin with the end of a clean nickel spatula.

Portions of the crude charcoal were transferred to silica basins, covered with pyrex clock glasses, and heated with the full flame of a Méker burner for forty minutes; to ensure uniform treatment, the charcoal was stirred every five minutes. During the first fifteen minutes or so inflammable vapour

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[1] See Bartell and Miller's method of preparation of sugar charcoal (J.A.C.S., 1922, 44, 1866).

was evolved and burned; tarry material also distilled on to the clock glasses. Finally the charcoal was thoroughly ground in a clean agate mortar, the first portion being rejected. All the crude charcoal was treated in this way and stored in a 500 ml. separating funnel fitted with a rubber stopper. The tap of the funnel was greased with only the merest trace of vaseline at the ends of the barrel, so that it could be turned without undue difficulty.

Approximately 4 lbs. of A.R. sucrose were converted into charcoal in the manner described. An ash determination was carried out by combustion of 1 g. portions in porcelain basins and a residue amounting to 0.04% by weight was found; a trace of iron could be detected in the residue. Later in the course of the research another 6 lbs. of A.R. sucrose was converted into charcoal in the same way. The ash content of this charcoal was also 0.04% and iron was again just detectable. This charcoal was stored in a bottle.

The first batch of charcoal prepared will be referred to as charcoal A and the second as charcoal B.

Preparation and Standardisation of Solutions

The solutions employed were prepared from A.R. (or Analytical Quality) chemicals and good distilled water, and stored in Jena glass bottles.

Deci-normal solutions of hydrochloric and nitric acids were used consistently. Standardisation was effected with A.R. sodium carbonate (dried), using methyl red as indicator, and boiling to expel CO_2 as the end-point was approached.

Initially 0.1N sodium hydroxide solution was used but when it was shown that the magnitude of the adsorption of sodium hydroxide by charcoal would vary too markedly with equilibrium concentration it was decided to work with 0.2N solution. The solution was prepared free from carbonate as follows:- a 16N solution of sodium bydroxide was allowed to stand in a large pyrex test-tube until the undissolved carbonate had settled out and a measured volume of the clear concentrated alkali diluted with CO_2-free distilled water to give the required concentration. The sodium hydroxide was standardised with the hydrochloric acid, using methyl red as indicator and boiling to eliminate traces of CO_2 when within a drop or two of the end-point.

Iodine in potassium iodide solution was prepared and standardised by means of A.R. arsenious oxide. At first 0.1N solution was used but as the capacity of some of the charcoals for adsorbing iodine proved great enough to produce almost complete decolourisation of the solution, it was later decided to work with 0.25N iodine solution.

Adsorption Procedure

Small quantities of charcoal were accurately weighed into pyrex tubes of about 75 ml. capacity, fitted with ground glass stoppers.[1] 25 Mls. of acid, alkali or iodine solution were introduced into each tube, the stopper inserted and coated with paraffin wax which served to seal the tube perfectly and to hold the stopper in position during shaking. The charcoal was shaken with the solutions for 24 hours by fixing the tubes radially to a slowly rotating circular wooden disc. Each adsorption determination was duplicated and six and sometimes eight tubes were shaken simultaneously. Between experiments the tubes were washed free from paraffin wax with very hot water, rinsed three times with distilled water and dried in an electric oven.

After shaking, the tubes were allowed to stand until most of the charcoal had settled out; the wax was then scraped off; the solutions decanted into pyrex centrifuge tubes, and centrifuged for a few minutes. Finally the solutions were decanted into pyrex test-tubes which were tightly stoppered with

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[1] The actual quantity of charcoal taken was at first 0.3 gm. in the case of all solutions but during the course of the research the procedure was altered somewhat and the quantity of charcoal taken in an adsorption experiment depended on the adsorbate solution and on how much charcoal was available. Tables will be given of the quantities of charcoal taken, together with the corresponding changes in titre.

cork stoppers soaked in paraffin wax. In this way the charcoal was separated from the solution quickly and efficiently. A very small quantity of charcoal always remained at the surface of the solution after centrifuging but it was left behind when solution was withdrawn by the pipette.

Measurement of Adsorptions

As soon as possible after the solutions had been transferred to the pyrex tubes, 10 ml. portions were measured out carefully with a pipette and titrated.[1] The acid solutions were titrated with sodium hydroxide, the sodium hydroxide with hydrochloric acid and the iodine with thiosulphate. The normalities of the standard solutions were made approximately half those of the adsorbate solutions and as it was just possible to take two 10 ml. portions for titration in each case, the titrations were duplicated. Preliminary trials without charcoal showed that no "blank" correction was necessary for any of the titrations. Hence the adsorption was obtained simply by subtracting the titre after shaking with charcoal from that obtained by titration of 10 ml. of the untreated solution. The burettes (30 ml.) and pipettes (10 ml. and 25 ml.) were of Grade B quality and the accuracy of calibration of each was checked before use. A lens was employed for reading the burettes.

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[1] Iodine solutions were titrated immediately.

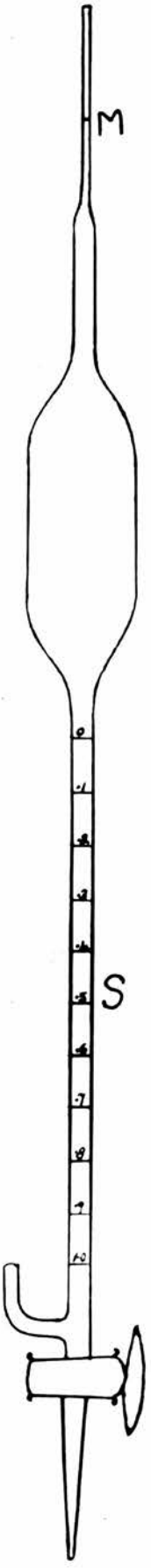

Fig. 1.

When the adsorption of hydrochloric acid was very small, its measurement by the above method was subject to a very considerable error (up to ±50%). At first the actual values of the hydrochloric acid adsorptions were not considered sufficiently important to warrant a more accurate method of determination. When, in later work, it became evident that more exact figures were required, the method was refined as follows.

The total volume of 0.05N sodium hydroxide solution required per 10 ml. portion of hydrochloric acid solution, was always about 20 ml. and only small changes in titre had to be measured. The burette shown in Fig. 1 (page 17) was therefore constructed. A 1 ml. graduated pipette, fitted with a stopcock and fine jet, was sealed to the bulb of a 20 ml. pipette and a piece of fine bore tubing (part of a 1 ml. pipette) with an etched mark (M) was joined to the stem of the pipette. The initial level of the sodium hydroxide solution was always adjusted to M and the concentration of the sodium hydroxide solution so chosen that in the titration of 10 ml. of untreated hydrochloric acid solution, the end-point was reached low down on the scale (S). In the titration of 10 ml. hydrochloric acid solution which had been shaken with charcoal, the end-point occurred at a reading higher up the scale. The difference between these two readings gave the change in titre produced by treatment of the

hydrochloric acid solution with charcoal.

As the scale (S) of the burette was graduated in hundredths of a millilitre and could be read to within 0.001 ml., it was obvious that the best results could only be obtained if the quantity of hydrochloric acid solution taken was measured more accurately than was possible by simple delivery from a 10 ml. pipette. The volumes of hydrochloric acid solution taken for titration were therefore weighed and all titres (in the case of HCl) referred to 10 g. of solution. The final adsorption was calculated on the assumption that 25 ml. 0.1N hydrochloric acid solution weighed 25 g., no significant error being thereby introduced. Titrations could now be duplicated to within 0.005 ml.

Treatment of Charcoal with Dry Air

Description of Apparatus

The final form of the apparatus employed for treating the charcoal with dry air is shown in Fig. 2a (page 20). The furnace tube, which had ground ends, was made of transparent silica (length 3 ft. 3 ins., internal bore 32 mm.) and could be evacuated by means of a Cenco Hyvac pump capable of yielding a vacuum of at least 0.001 mm. In order to get the best results from the pump it was decided to restrict to a minimum the amount of rubber used in the vacuum line. The short piece of rubber tubing XY was necessary to give a certain degree of flexi-

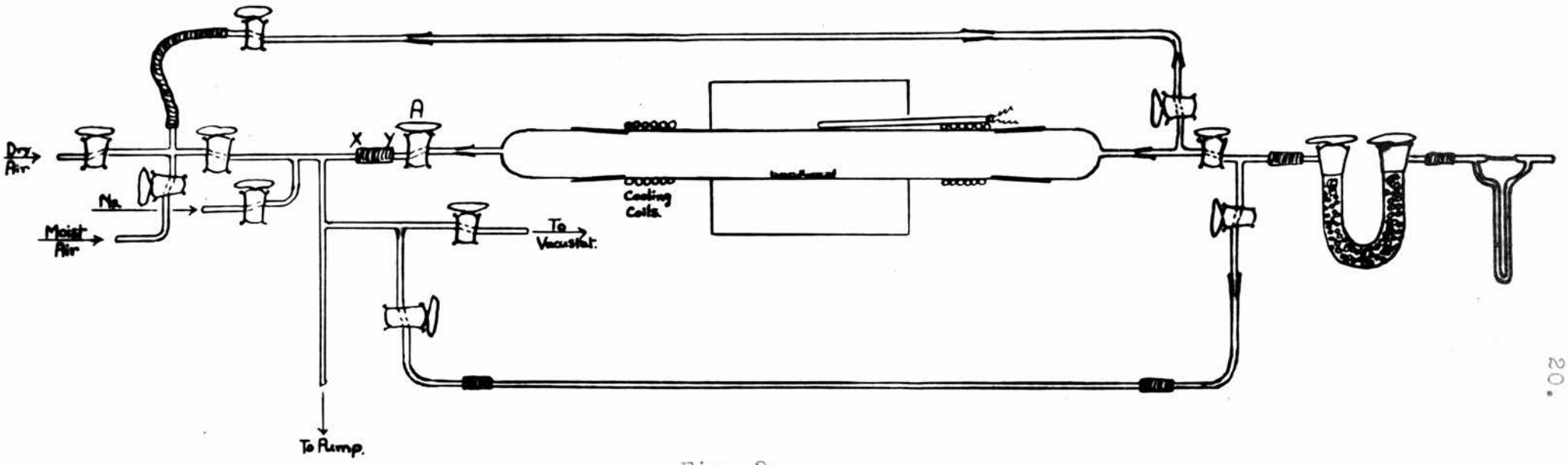

Fig. 2a

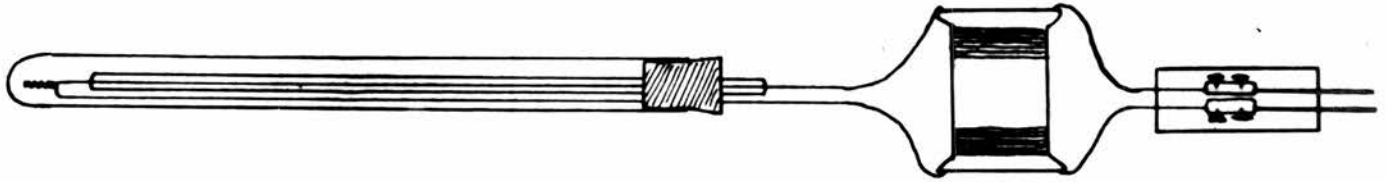

Fig. 2b

bility but it could be isolated from the furnace tube by the stopcock A. All the stopcocks and joints were lubricated with Edwards Apiezon L grease. The furnace tube joints were kept cool by wrappings of cotton wool saturated with cold water and by the action of cooling coils.

The Gallenkamp furnace employed was operated in conjunction with a "Sunvic" furnace control unit which enabled temperatures from about 350° to 1000° to be obtained and it was found that any particular setting of the control unit would maintain a steady temperature. A calibration of the temperature regulator was made in order to ascertain approximately what regulator setting would be required for the maintenance of any desired temperature. Thereafter the furnace could be heated up with the full current until the desired temperature was almost reached and then, by adjusting the regulator, this temperature could be maintained.

Temperatures were measured by means of a thermocouple, made from a suitable combination of two nichrome wires (Ferry and Bright Ray), and calibrated against a Cambridge platinum/platinum-rhodium thermometer. The pyrometer was constructed as shown in Fig. 2b (page 20). The "hot-junction" was made simply by twisting the two wires together, while the "cold junction" (room temperature) was made by joining the wires to copper leads, insulating them from one another and wrapping the whole

in asbestos string. As the hot junction had to be renewed periodically, a considerable reserve of each wire was wound on a bobbin before being joined to the copper leads.

The e.m.f. produced by the thermocouple was measured by means of a Cambridge valve electrometer. The plot of temperature against e.m.f. gave a very good straight line and temperatures could be read to at least $\mp 10^{\circ}$.

The treatment of the charcoal was effected by heating it in a stream of air, a steady flow of which was obtained by running water from a constant head device into a 20-litre bottle (see Fig. 3, page 23). The two taps A and B served to regulate the rate of inflow of water. With tap A fully open, tap B could be adjusted to give the desired rate of passage of gas, as measured by the flowmeter attached at the exit of the apparatus. Tap B need not then be touched again, tap A being used to stop the flow of water into the bottle when required. When it was desired to pass a stream of N_2 or O_2, the 20-litre bottle was first completely filled with water and the water then expelled by introducing the gas under pressure, from a cylinder.

The air was freed from acid gases by bubbling it through 10% aq. NaOH, and dried by passage through conc. H_2SO_4, calcium chloride (one U-tube), and finally over phosphorus pentoxide (75 cm.). At the exit end of the apparatus a U-tube of calcium

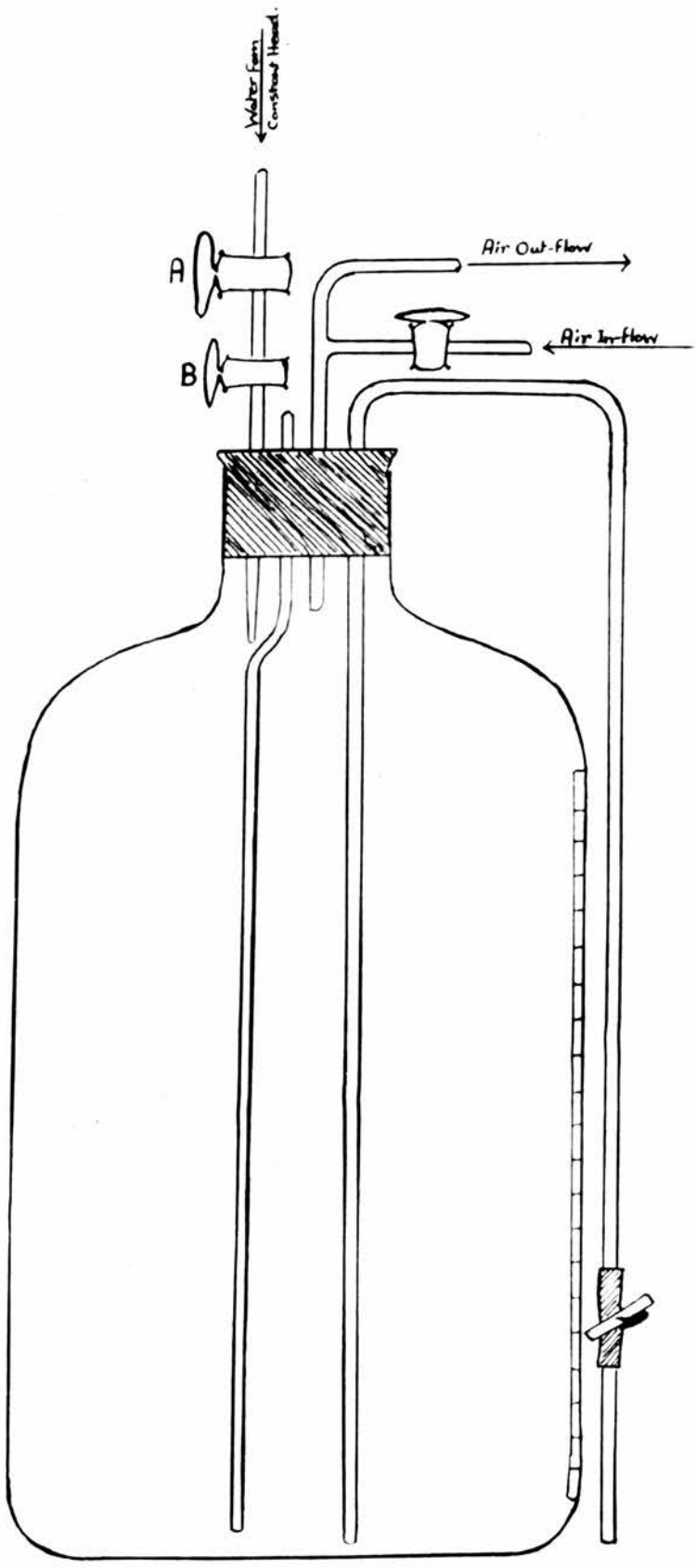

Fig. 3.

chloride prevented backward diffusion of water vapour into the furnace tube.

Procedure

It was decided to evacuate samples of charcoal A at a temperature of about 800° and then without removing them from the furnace, proceed to heat them in a stream of carefully dried air at the required temperature. In this way no opportunity would be given for the charcoal to pick up water after evacuation.

The final method of treatment with air was adopted as a result of a series of preliminary experiments designed to ascertain the optimum conditions for obtaining the maximum yield of uniformly activated charcoal. Portions (2 g.) of charcoal were weighed into 2 silica boats, which were numbered, the boats pushed into the heart of the furnace tube and the assembly of the apparatus completed. The furnace tube was evacuated and nitrogen (from a cylinder) introduced cautiously until the pressure was restored to atmospheric; then allowed to stream through at a moderate rate, a small pulsimeter containing sulphuric acid replacing the flowmeter during this operation. The furnace was switched on and after roughly 45 mimutes on full current the temperature was raised to about 825°, whereupon the regulator was turned back to the setting required to maintain this temperature.

While the furnace was heating up, an appreciable amount of water was evolved from the charcoal and condensed at the cold ends of the furnace tube.

Passage of nitrogen was continued for a further 15 minutes, then stopped and the oil pump switched on. The stopcock (A) between the pump and the rest of the apparatus had to be opened cautiously otherwise charcoal was liable to be expelled from the boats. Pumping was continued for 6 hours at the steady temperature of 825°, at the end of which period the stopcock A was closed again.[1] The pump and furnace were switched off and the latter allowed to cool overnight.

Before introducing the dry air the furnace was brought to the desired temperature with the pump in action, any gas desorbed by the charcoal being drawn away. At the lower temperatures of treatment the pressure could now be maintained at about 0.01 mm. The introduction of the dry air was proceeded with very carefully and sudden rushes of air into the furnace tube were strictly avoided lest incomplete elimination of moisture should result. Generally about an hour was required to restore the pressure

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[1] The vacuum obtained after 6 hours pumping at 825° was about 0.2 mm. As it was unlikely that the quartz tube would become porous to any significant extent at 825°, failure to reach a lower pressure indicated that the charcoal must be degassing very slowly. When cold the pressure in the furnace tube was down to less than 0.001 mm. so that there were no leaks in the apparatus. This very low pressure was due, of course, to re-adsorption of the gas in the tube by the charcoal as it cooled down.

within the apparatus to atmospheric. A slow stream of dry air was then passed at the steady rate of 10 ml. per min.[1] for 24 hours, the air flowing for 12 hours in the direction left to right over the charcoal and for the remaining 12 hours, from right to left. Under these conditions the amount of activation taking place in each boat was kept more or less the same and the volume of air passed during 24 hours ensured that the charcoal would be well activated.

After treatment in this way the furnace was switched off and the charcoal removed, a long pyrex rod, bent at one end to form a small hook, being used to draw out the boats and a piece of tin-plate to lift them clear of the greased joint. The boats were placed immediately in a desiccator and, when cold, were weighed. The charcoal was then transferred to a small clean bottle, closed with a rubber stopper, and after thorough mixing, small quantities were weighed into the pyrex tubes. The solutions of acid, alkali and iodine were then introduced and the adsorptions determined in the manner already described.

The conditions under which the charcoal was treated with dry air resulted in approximately the same amount of activation taking place in each boat.

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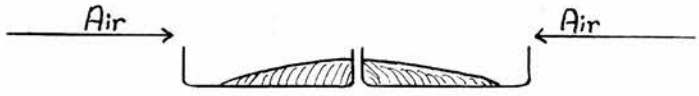
[1] At this rate of flow the drying of the air by the reagents employed would be very thorough (cf. Farkas and Melville, "Experimental Methods In Gas Reactions" (1939), page 149).

At temperatures above 400° the loss in weight became fairly constant at about 45-55%.

As the temperature of treatment was raised the adsorption of iodine showed a regular increase, as expected, except in the case of the two treatments carried out at 520° and 525° when there was a fall as compared with the treatment at 475°. This irregularity may be accounted for by the fact that at 500° the rate of combustion became very rapid, that portion of the charcoal in each boat, over which the stream of air first passed, being completely burned away, as shown in the diagram below.



The gas passing on is so denuded of oxygen, owing to the rapid rate of combustion, that progressively less activation of the remainder of the charcoal in the boat takes place. The effect of raising the temperature from 475° to 520° and 525° on the vigour of the activation may not compensate for the decrease in oxygen available for activation. In the treatment at 750°, however, the increased vigour of activation apparently predominates, but it should be noted that at this high temperature carbon dioxide formed in the combustion would also behave as an activating agent.

The results of these experiments are given in

Tables II(a),(b),(c) on pages 51-53.

Preliminary Experiments

The earliest experiments were carried out with larger quantities of charcoal, contained in 5 silica boats (1.5 g. in each), and the apparatus was designed so that the passage of air was possible in only one direction. The results obtained from these experiments are given in Tables I(a),(b) on page 29.

From Table I(a)(the loss in weight which took place in each boat is recorded) it will be seen that the loss in weight was greatest in boats 1 and 2, which were nearest the end at which the stream of air entered the furnace tube, and fell off progressively in succeeding boats. The differences became more marked as the temperature of activation was raised, since the rate of combustion of the charcoal increases and a higher proportion of oxygen is removed from the air stream by the charcoal in the first two boats.

In Expt. 1 of Table I(b), the adsorption values are those with a sample of charcoal A which had been evacuated at 825° for 6 hours; the adsorption of alkali is zero, whereas there is quite a strong adsorption of acid. The adsorption values in the succeeding experiments were obtained with samples of charcoal A which, after evacuation, were treated with dry air. It is evident that treatment

Table I (a)

Expt.	Treatment of Charcoal	Loss in wt. (%)					Overall loss (%)
		Boat 1	Boat 2	Boat 3	Boat 4	Boat 5	
1	Evacuated for 6 hrs. at 825°	-	-	-	-	-	-
2	Evacuated, then heated in dry air for 24 hrs. at 355°	21.3	21.0	16.1	11.9	8.5	15.7
3	As above, at 415°	45.9	29.5	13.1	8.8	(8)*	21.0
4	" " " 470°	66.7	34.5	13.6	9.2	9.0	26.0
5	" " " 410° (air passed for 12 hrs. in each direction)	24.9	13.0	14.0	22.5	-	18.6

* A little charcoal was spilt from boat 5 during its removal from the furnace. The loss value given (8%) is a reasonable estimate made in order to calculate the overall loss with fair accuracy.

Table I (b)

Expt.	Equivalents adsorbed per g. charcoal ($\times 10^5$)							
	HCl		HNO_3		NaOH		Iodine	
1	33	(Mean)	69	(Mean)	0	(Mean)	371	(Mean)
	35		72		0			
		34		71		0		
2	9		32		138		482	
	8		33		138			
		8.5		32.5		138		
3	12		45		106		457	
	13		44		107		446	
		12.5		44.5		107		452
4	18		55		54		395	
	18		54		57		393	
		18		54.5		55.5		394
5	7		36		137		494	
	7		36		138		497	
		7		36		138		496

with dry air has reduced the adsorption of acid and resulted in the appearance of a marked adsorption of alkali. However, the results might appear anomalous in the sense that while the overall percentage loss in weight increases, the iodine adsorption decreases, indicating a corresponding decrease in the specific surface area of the charcoal. The loss in weight for individual boats explains this apparent anomaly. On mixing, the more highly activated charcoal from the first two boats is diluted with less highly activated charcoal from the other three. The effect of dilution becomes accentuated as the temperature is raised, for progressively smaller amounts of highly activated charcoal are mixed with progressively larger amounts of less highly activated charcoal. The total loss in weight is greatest in the case of the activation carried out at 470°, but the iodine value is not much different from that of the evacuated charcoal.

To overcome this difficulty the activation apparatus was modified so that the air could be streamed over the charcoal in either direction (see Fig. 2a, page 20). The same weight of charcoal was divided equally between only four boats and the air was streamed for 12 hours in each direction. One experiment (Expt. 5, Tables I (a), (b)) was carried out under these conditions, at a temperature of 410°. Since more uniform treatment of the charcoal was

achieved by the modifications introduced, it seemed likely that the employment of only two boats would lead to still further improvement, and this procedure, therefore, was adopted in all later work.

Treatment of Charcoal A with Moist Air

Except for the use of moist air, the procedure was the same as that employed in the case of dry air (see page 24). Air (from the 20-litre bottle) was bubbled through conc. H_2SO_4, then through 10% aq. NaOH and finally moistened by passage through a dreschel bottle filled with glass beads covered with water at room temperature. The rate of passage of air was again 10 ml. per minute. During the course of the treatment condensation of water at the ends of the furnace tube below the cooling coils indicated that the air was effectively moistened. The calcium chloride U-tube was disconnected from the exit end of the apparatus during these activations.

The data obtained from these experiments are shown in Tables II (a), (b), (c) on pages 51-53.

Treatment of Charcoal A with Moist and Dry Nitrogen

Nitrogen from the 20-litre bottle (see page 22) was bubbled through conc. H_2SO_4, through 10% aq. NaOH and finally moistened in the manner described above.[1] The gas was then streamed for 12 hours in

[1] Air was displaced from the wash-bottles by passing a stream of nitrogen from a cylinder for about 30 minutes.

each direction at 10 ml. per min. over a portion of charcoal A (previously evacuated for 6 hours at 825°) which was kept at a steady temperature of about 400°. For comparison, an experiment was performed in which the evacuated charcoal was heated under the same conditions in a stream of dry nitrogen.

The data obtained in these experiments are presented in Tables III (a), (b), (c) on page 58.

Degassing of Air-Treated Charcoal (D-series)

Samples (4 g.) of charcoal A were evacuated at 825° for 6 hours and then treated for 24 hours at a temperature producing a very marked adsorption of sodium hydroxide; actually the temperature varied between the limits 425°-440°. Immediately after treatment, the furnace tube was evacuated and the furnace raised to, and maintained at, some new temperature. The temperature and/or the time of degassing were varied from experiment to experiment, and when the period of degassing was long the pump was not kept in action continuously, but gas was removed periodically as it accumulated.

In one experiment (D_1) the charcoal was heated in a vacuum at the same temperature as that at which it had been treated with air. After 24 hours heating the lowest pressure reached was 0.05 mm. despite prolonged periods of pumping. Slow desorption of gas must therefore have been taking

place. At higher degassing temperatures it was uniformly observed that the pump would quickly evacuate the furnace tube to about 0.1 mm. before any appreciable evolution of gas from the charcoal took place. However, as the temperature rose the pressure increased, despite the action of the pump, to a few millimetres, fell again when the temperature ceased to rise, but could not be reduced below 0.1 - 0.05 mm. even after long periods of evacuation. When air-treated charcoal was degassed at 750° and 825° it was observed that as the temperature increased from about 550° to 650° a very rapid evolution of gas took place as indicated by the sudden change in the action of the pump. The pressure increased to as much as 5 mm. but began to fall slowly again even although the temperature was rising. It appeared that the bulk of the desorbable gas came off all at once as the temperature rose from 550°-650°.

The treatment of the charcoal used in the experiment (D_{10}) carried out at 825° was slightly different from the rest. Only 2 g. of charcoal A remained and in order to make use of it, yet keep the experimental conditions uniform, it was treated with air in one boat along with 2 g. of another batch of charcoal in a second boat. The use of two boats allowed the treatment to be continued for 24 hours. Both charcoal samples were degassed, but were kept separate, and the adsorption experiments carried out with the one prepared from charcoal A.

The appearance of the charcoal after degassing at a high temperature is worthy of note. The surface was covered with cracks and the effect was most marked in the case of the charcoal degassed at 825°.

In the above experiments the period of heating could not be reduced below a certain minimum time. After the pump and furnace had been switched off, the vacuum had to be broken by admitting nitrogen and about 15 minutes always elapsed before the charcoal could be removed and placed in a desiccator to cool.

The data for these experiments are recorded in Tables IV(a),(b),(c) on pages 60-62.

Preparation of Hexaiodobenzene

Hexaiodobenzene was chosen as a suitable material from which to prepare hydrogen-free charcoal (Riley, J.C.S., 1946, 456). The synthesis of this compound, due to Rupp (Ber., 1896, 29, 1631), is as follows: benzoic acid (3 gm.) is dissolved in fuming sulphuric acid (30 gm.) at 120° and iodine (20 gm.) added over a period of half-an-hour with continual stirring; the reaction mixture is then heated at 180° for 6 hours. After allowing the flask to cool, the contents are poured into water, the hexaiodobenzene which separates is filtered off and freed from excess iodine by heating on a water bath in a current of air; any iodinated benzoic

acid is removed by extraction with sodium hydroxide solution. The dried crude product is recrystallised from nitrobenzene and is obtained as reddish brown needles.

It was decided to work with larger quantities of reactants and preparations were carried out using 15-18 gm. benzoic acid and corresponding weights of iodine and fuming sulphuric acid. The time taken over the addition of the iodine was suitably protracted and the period of heating at 180° was increased to 12 hours. When a quantity of crude hexaiodobenzene had been accumulated it was recrystallised from nitrobenzene and the product (120 gm.) was analysed for hydrogen. Analysis showed that the product was not entirely free from hydrogen (0.15% found) and possibly, owing to the increased scale of the preparation, the product contained some incompletely iodinated benzene.

Recrystallisation from nitrobenzene was not an easy matter as the compound starts to separate out almost immediately the solvent ceases to boil. Moreover, because of the very low solubility of the compound, the recrystallisation had to be carried out in many stages and was therefore a tedious process. Complete removal of the nitrobenzene was also a difficulty and despite thorough washing by refluxing with chloroform, followed by drying overnight in an oven at 100°, a trace of solvent still adhered to the substance. The nitrobenzene was

apparently occluded and diffused out slowly after the compound had been standing for a time, as the smell of nitrobenzene became more perceptible the longer the compound was stored. The presence of a trace of nitrobenzene was actually proved when a portion of the compound was charred.

Before attempting to purify the hexaiodobenzene any further it was considered advisable to convert a quantity of the compound into charcoal and test whether it would display similar properties to sugar charcoal. A portion (30 gm.) of hexaiodobenzene was converted into charcoal and experiments with it showed that its behaviour towards solutions of hydrochloric acid and sodium hydroxide could be influenced by the conditions of treatment just as in the case of sugar charcoal. It was desirable, therefore, that the remaining hexaiodobenzene should be purified further in order to eliminate hydrogen as far as possible.

It was found that hexaiodobenzene could be recrystallised equally well from o-dichlorobenzene and it was decided to use this solvent rather than nitrobenzene. After recrystallisation the hexaiodobenzene was filtered and washed free from o-dichlorobenzene by refluxing with chloroform followed by drying overnight in an oven at 180°. A sample of the product after this treatment was analysed and once again a small percentage of hydrogen (0.39%) was found. Experiment showed that the compound did

not pick up moisture so that hydrogen from that source must be ruled out. The accuracy of the determination probably was not sufficient to make the slight increase in the percentage hydrogen significant. However, although it had not been possible to eliminate the hydrogen altogether, the percentage of hydrogen present in the product was very low. Moreover, it appeared very probable that the bulk of the hydrogen would be eliminated on charring the compound. It was decided, therefore, to proceed with the preparation of charcoal and to analyse a portion of it for hydrogen.

Preparation of Hexaiodobenzene Charcoal

The decomposition of the hexaiodobenzene was effected at a relatively low temperature in order to minimise the risk of introducing silica into the resulting charcoal through interaction of the iodine evolved with the walls of the furnace tube and the boats in which the compound was contained. Riley (J.C.S., 1946, 459) found that the charcoal he obtained by charring at 1000° contained silica, and he suggested that this was due to contamination of the charcoal with silicon iodides, formed by such interaction. These iodides would be hydrolysed to silica on exposure to the atmosphere.

The apparatus used to prepare the charcoal is shown in Fig. 4 (page 38). A pyrex furnace tube with ground ends was used and in order that the

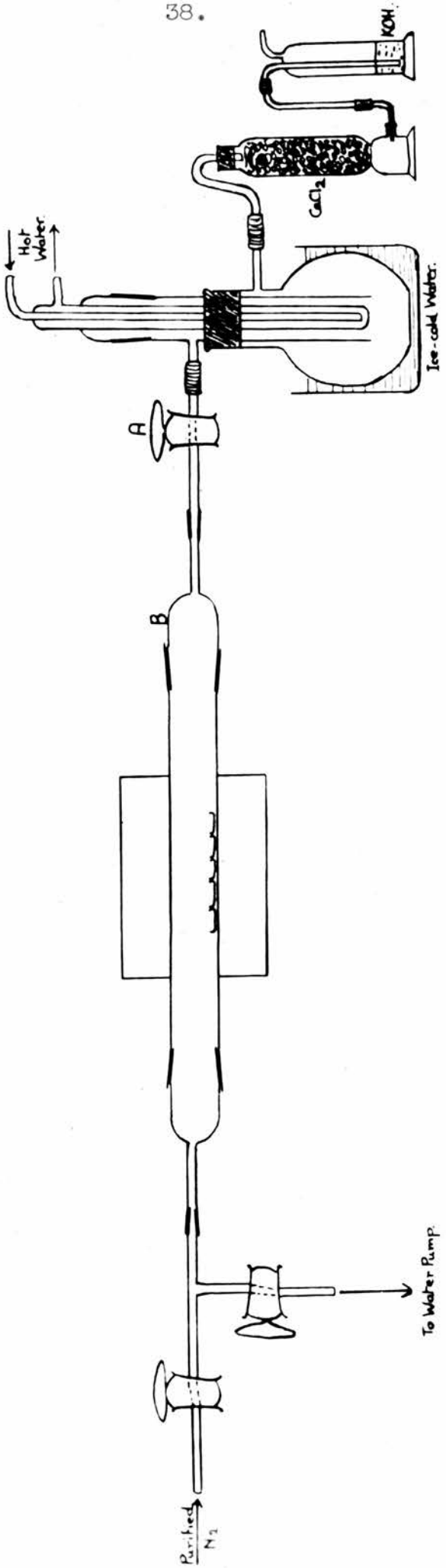

KOH
$CaCl_2$
Hot Water
Ice-cold Water
A
B
To Water Pump
Purified N_2

Fig. 4

joints might be kept hot, a silicone grease which operated efficiently up to 200° was employed. Temperatures were measured with a mercury (in silica) thermometer.

In the first preparation of charcoal, 30 g. of hexaiodobenzene (contained in 5 silica boats) was placed in the furnace tube and the tube evacuated with a water pump; a liquid-air trap prevented any backward diffusion of water vapour from the pump into the apparatus. Nitrogen (from a cylinder), freed from traces of hydrogen and oxygen by passage over heated copper oxide (25 cm.) and copper gauze (30 cm.), from CO_2 by bubbling through 10% aq. NaOH and from water vapour by passage through conc. H_2SO_4 and over phosphorus pentoxide (3 ft.), was introduced cautiously into the furnace tube and allowed to stream at moderate speed through the entire apparatus for about an hour. The calcium chloride tower prevented backward diffusion of water vapour from the atmosphere. Any adsorbed water was removed from the hexaiodobenzene by heating the compound in the furnace to 200°, with the pump in action, and maintaining that temperature for 2 hours. The furnace tube was then "rinsed" three times with purified nitrogen by alternate admission of the gas and evacuation. Finally purified nitrogen was streamed through the apparatus, the temperature raised slowly to 450° and maintained at about that figure.

It was noted that while the furnace was heating

up, several tiny droplets of an oily liquid, smelling of nitrobenzene, collected in the liquid-air trap.

When the hexaiodobenzene began to decompose, the liberation of iodine caused a sudden increase of pressure which, however, was quickly relieved by condensation of the iodine at the cold ends of the furnace tube. A certain amount of sublimation of the compound was also observed at this stage. It had been anticipated that the iodine vapour would tend to condense in the exit tubes and clog them and for that reason the flask immersed in ice-cold water was included to act as a trap. The glass tubes (including the large stopcock A) leading to the flask were made of pyrex and could be heated to facilitate the passage of the iodine vapour into the trap. However, it was actually found that almost all the iodine condensed at the ends of the furnace tube and could be made to pass on into the trap only with great difficulty; the inclusion of this trap thus provided no advantage. After 6 hours heating in streaming nitrogen, the passage of gas was stopped, the stopcocks closed and the furnace allowed to cool overnight.

When the furnace was cold the pressure was restored to atmospheric by admitting more nitrogen. Practically all the iodine had condensed in the ground end B (see Fig. 4, page 38), so that when the furnace tube was opened the boats could be drawn out easily. The charcoal was ground in a clean agate

mortar, the first small portion being rejected, and 3.5 g. obtained.

This charcoal still contained some iodine and was therefore further treated as follows. After thorough cleaning,[1] the apparatus was reassembled and the charcoal, contained in two silica boats, introduced again. The furnace tube was "rinsed" with purified nitrogen and the temperature raised to 550° with the pump in action. More iodine came off and condensed at the cold ends of the tube but by frequently warming the ends with a bunsen flame to volatilise the iodine, most of it was slowly sucked away by the pump. After 6 hours heating at 550° the furnace was switched off and allowed to cool overnight. The vacuum was broken by admitting nitrogen and the boats withdrawn. The charcoal (2.5 g.) was stored over calcium chloride and sodium hydroxide in a vacuum desiccator (evacuated to 0.01 mm.) for one month before use.

In the second preparation of hexaiodobenzene charcoal, two batches of 35 g. of the compound were charred in the manner just described (iodine-trap omitted). As iodine was known to remain in the charcoal after the 6 hours heating at 550°, in this preparation it was further heated at 825° for 4 hours in vacuo (2 hours with the water pump in

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[1] It was observed that the part of the furnace tube which had been in the heart of the furnace was covered with a deposit of carbon. This deposit probably resulted from sublimation followed by charring.

action and then 2 hours with the oil pump operating). The charcoal (5.2 g.) finally obtained was stored in a vacuum desiccator for a fortnight before being used.

The first and second preparations of hexaiodobenzene charcoal will be referred to respectively as H_1 and H_2.

Experiments with Hexaiodobenzene Charcoal

The following experiments were carried out with the 2.5 g. of charcoal H_1.

Charcoal H_1^e.

A portion (1 g.) of charcoal H_1 was weighed into a silica boat and evacuated for 6 hours at 825°, as in the sugar charcoal experiments. During the preliminary heating in nitrogen up to 825° a small quantity of iodine was evolved, but on evacuation this was quickly removed and condensed in a liquid-air trap. Some of the charcoal was also ejected from the boat at this stage and an appreciable quantity lay in the part of the tube outside the furnace. After 6 hours evacuation at 825° the stopcock A (Fig. 2a, page 20) was closed and, after cooling overnight, the vacuum was broken by admitting nitrogen. About 0.25 g. charcoal remained in the boat and was used in an adsorption experiment with 0.1 N sodium hydroxide. The charcoal (about 0.6 g.) lying in the furnace tube was removed, thoroughly mixed and about 0.25 g. portions

used for sodium hydroxide and hydrochloric acid adsorption experiments.

Charcoal H_1^o.

What remained of charcoal H_1 (1.5 g.) was weighed out into a silica boat and evacuated for 6 hours at 825°. After the preliminary heating in nitrogen the pressure in the furnace tube was reduced very slowly but despite this precaution some charcoal was again ejected from the boat. On this occasion, however, only a light dusting of charcoal appeared in the exposed part of the furnace tube. The furnace was allowed to cool overnight as usual; then raised to 430° with the pump in action; and when the temperature had settled down the pump was switched off and dry air slowly admitted until the apparatus was filled with dry air at atmospheric pressure. The treatment was continued for a total of 6 hours, the air being streamed over the charcoal for 3 hours in each direction. The charcoal was then removed from the furnace, cooled in a desiccator, and weighed; whereupon it was transferred to a small bottle fitted with a rubber stopper and thoroughly mixed. Two portions (0.25 g.) were used for sodium hydroxide adsorption determinations and another portion (0.3 g.) was used for a hydrochloric acid determination. When the furnace was cold the charcoal lying in the furnace tube was carefully swept out and weighed in order that an estimate might be made of the loss in weight

resulting from the evacuation and treatment.

Experiments of the same type were carried out with charcoal H_2 but because of the tendency for some of the charcoal to be expelled from the silica boats when evacuating the apparatus at a high temperature, it was decided instead to heat the charcoal for 6 hours at 825° in a stream of purified nitrogen. The nitrogen was purified by passage over heated copper oxide (28 cm.) and copper gauze (37 cm.), through conc. H_2SO_4, then over phosphorus pentoxide (75 cm.) and finally through a liquid-air trap.

Charcoal H_2^e.

A portion (1.8 g.) of charcoal H_2 was introduced into the furnace, the apparatus evacuated and purified nitrogen admitted. The temperature was raised to 825° and kept at that temperature for 6 hours, nitrogen streaming all the time. Once again a little iodine was evolved as the temperature rose to 825° and the sulphuric acid in the pulsimeter at the exit end of the apparatus was tinged violet. The evolution of iodine appeared to cease after a short time and at the end of the 6 hours the sulphuric acid in the pulsimeter was quite colourless. When the furnace was cold the charcoal was removed; the loss in weight determined; and adsorption experiments carried out in the usual way.

Charcoal H_2^o.

A second portion (3.4 g.), contained in two

silica boats, was heated in nitrogen in the manner just described. The nitrogen was then pumped out carefully in the cold (without scattering the charcoal) and dry oxygen introduced slowly after the furnace had been raised to 400°. The oxygen was passed at the steady rate of 10 ml. per min. for a period of 8 hours (4 hours in each direction). The charcoal was removed from the furnace after this treatment and adsorption experiments carried out immediately, using 0.2 N sodium hydroxide, 0.25 N iodine and 0.1 N hydrochloric acid.

The increased rate of combustion in oxygen was very marked. Almost 80% of the charcoal was lost during treatment and what remained in the boats was reduced to a very fine, black powder.

The data obtained from these experiments with hexaiodobenzene charcoal are given in Tables V (a), (b), (c) on pages 65-66.

The Hydrogen Content of Evacuated Sugar and Hexaiodobenzene Charcoal

The hydrogen content of evacuated sugar charcoal (L^e) and hexaiodobenzene charcoal (H_2^e) was determined by complete combustion and absorption of the liberated water, adsorbed water having been previously removed by heating at 840° in nitrogen.[1] Two pairs of U-tubes containing calcium chloride[2]

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[1] The oxygen and nitrogen were purified as described on pages 78 and 83.

[2] The calcium chloride was rendered inert to CO_2 before use. Cf. Quantitative Chemical Analysis (Cumming and Kay) 8th ed., page 290.

were employed to absorb water, the first (A and B), when nitrogen was the streaming gas and the second (C and D), for the combustion. Before use, A and B were flushed out with nitrogen and C and D with oxygen. This precaution was necessary as the replacement of one gas by the other produced a measurable change in weight. Before weighing, the absorption tubes were allowed to hang beside the balance for half-an-hour.

The procedure adopted was identical for the two specimens of charcoal and may be summarised as follows. A quantity (0.3 g.) of charcoal, contained in a silica boat, was placed in the furnace tube, the apparatus evacuated and nitrogen introduced slowly. With U-tube A in position (see Fig. 5, page 47), the furnace was heated up to 840° and the nitrogen passed at 20-25 ml. per min. for 1½ hours. U-tube A was then disconnected, B attached in its place and the passage of nitrogen continued for 1 hour; whereupon B was replaced by C. Before proceeding with the combustion the temperature was reduced to about 600° by allowing the furnace to cool in the nitrogen stream for 30 minutes. Passage of nitrogen was then stopped and oxygen streamed in its place at about the same rate. After 4 hours U-tube C was replaced by D and the passage of oxygen continued for a further ½-hour.

Because of the difficulty experienced in removing iodine completely from the hexaiodobenzene

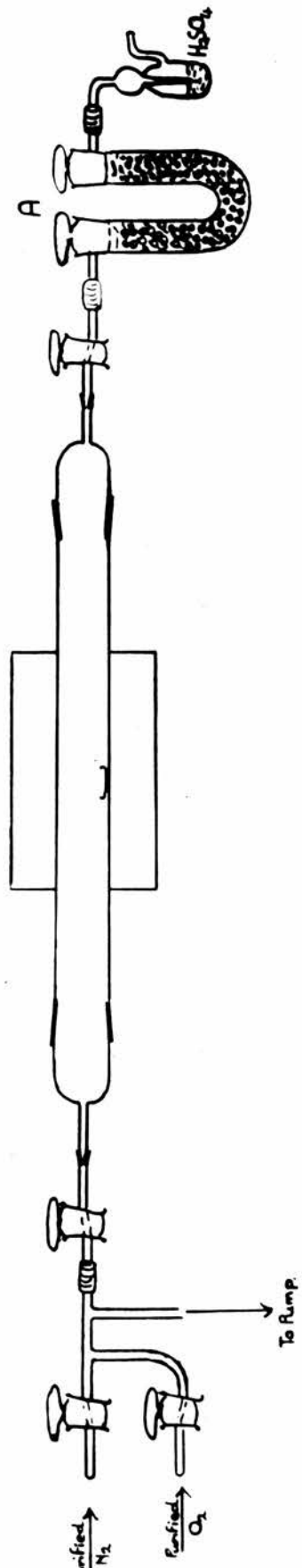

Fig. 5

charcoal, it was considered advisable to test whether or not any iodine was liberated when this charcoal was burned, since iodine vapour present in the oxygen stream would tend to adhere to the calcium chloride. Only a small quantity of charcoal H_1^e was available for this purpose and in order to make it comparable with H_2^e it was first heated for 2½ hours at 840° in a stream of nitrogen, after which the charcoal was weighed and then treated as described above. In this experiment, instead of passing the emergent oxygen stream through calcium chloride, it was bubbled through 15 ml. 10% potassium iodide solution. After 2 hours the test-tube containing the solution was disconnected, the solution transferred to a conical flask and titrated with 0.001 N sodium thiosulphate. A fresh solution of potassium iodide (15 ml.) was placed in the test-tube and oxygen allowed to pass through it for 2 hours. It was then titrated as before with sodium thiosulphate. A "blank" titration was also carried out on 15 ml. potassium iodide solution which had simply stood for several hours.

The results of these experiments are given in Table VI on page 68.

In agreement with Ockrent (J.C.S., 1934, 291), it was found that the quartz furnace tube gave up a small amount of water when heated at a high temperature. It was therefore heated at 800° - 850° and then cooled in a stream of purified nitrogen prior to

these experiments. In later work involving the quantitative determination of water, the furnace tube was similarly treated before use.

RESULTS and DISCUSSION

The Adsorptive Properties of Charcoal treated with Dry Air at Various Temperatures and the Influence of the Presence of Water Vapour in the Air

The method finally employed for treating the charcoal with dry air has been described on page 24 and the data recorded in columns 4 and 5 of Table II (a) (page 51) show that the procedure ensured a fairly uniform action upon the two samples of charcoal treated in any instance. By following the procedure strictly in each case and keeping the rate of flow of air as nearly constant as possible, the temperature of treatment became the only variable affecting the adsorbing properties of the charcoal. Table II (b) gives the data obtained in the actual adsorption measurements, while in Table II (c) the adsorptions are expressed as equivalents per g. charcoal ($x10^5$). The adsorption of iodine is taken as a measure of the surface area and the ratio of acid or alkali adsorbed to iodine adsorbed is regarded, therefore, as the adsorption per unit area, i.e. the area required for the adsorption of an equivalent of iodine.

According to Ockrent[i] the adsorption of sodium hydroxide is due to the presence of a high-temperature adsorbed layer of water, while hydrochloric acid is taken up by charcoal freed from such water. In support of his contentions he points out that Kolthoff[ii] and Miller[iii] stress that the presence of

The Adsorptive Properties of Charcoal treated with Dry and Moist Air

Table II (a) - Treatment of Charcoal

Charcoal	Treatment	Vol. air passed (l.)	Loss in wt. (%)		Overall loss (%)
			Boat 1	Boat 2	
C_1^e	Charcoal A evacuated for 6 hrs. at 825°	-	9.4	9.1	9.2
C_2^e	As above	-	11.1	-	11.1
C_1	C_1^e heated for 24 hrs. in dry air at 370°	13.5	24.3	23.2	23.7
C_2	As above, 370°	14.0	27.2	25.7	26.4
C_3	C_1^e heated for 24 hrs. in moist air at 370°	13.8	24.8	25.8	25.3
C_4	As above, 370°	14.8	26.0	28.8	27.4
C_5	C_1^e heated for 24 hrs. in dry air at 440°	15.0	45.6	48.6	47.1
C_6	As above, 440°	14.8	47.3	53.2	50.2
C_7	" " 475°	15.0	51.0	51.5	51.2
C_8	" " 525°	-	59.1	52.0	55.5
C_9	" " 520°	-	54.3	47.1	50.1
C_{10}	" " 750°	16.0	56.2	53.2	54.8

Table II (b) - Adsorption Data (Experimental)

Charcoal	Wt. Charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 ml. HCl. (ml. 0.05N NaOH)	Wt. Charcoal shaken with 25 ml. 0.1N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.05N HCl.)	Wt. Charcoal shaken with 25 ml. 0.1N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.05N $Na_2S_2O_3$)
C_1^e	0.3000 0.3015	0.72 0.76	0.3005 0.3004	0.00 0.00	0.3006 0.3016	6.97 7.28
C_2^e	0.3026 0.3009	0.77 0.76	0.2998 0.2884	0.00 0.00	0.3022 0.3014	8.25 7.95
C_1	0.3002 0.3016	0.13 0.13	0.3009 0.3003	5.05 5.06	0.3008 0.3003	12.82 12.86
C_2	0.3001 0.3010	0.12 0.13	0.3009 0.3012	5.33 5.23	0.3008 0.3005	12.80 12.85
$^{*}C_3$	0.3008 0.3010	0.09 0.10	0.3021 0.3003	5.26 5.22	0.3009 0.3002	12.68 12.69
$^{*}C_4$	0.2997 0.2997	0.07 0.07	0.3011 0.3007	5.65 5.58	0.3004 0.3008	13.06 13.07
C_5	0.3005 0.3015	0.05 0.07	0.3018 0.3005	6.20 6.18	0.3017 0.3010	13.21 13.19
C_6	0.3006 0.3011	0.08 0.08	0.3024 0.3005	6.26 6.25	0.3001 0.3005	13.10 13.18
C_7	0.3010 0.2997	0.16 0.14	0.3006 0.3021	5.02 5.03	0.3005 0.3018	14.34 14.36
C_8	0.2940 0.2668	0.31 0.28	0.3010 0.3046	1.55 1.69	0.3016 0.3038	13.00 13.05
C_9	0.3007 0.3016	0.42 0.44	0.3010 0.3017	1.16 1.22	0.3012 0.3018	12.31 12.47
C_{10}	0.3000 0.2956	0.98 0.97	0.3004 0.3009	0.17 0.16	0.2998 0.2998	18.85 18.85

* Charcoal treated with moist air.

Table II (c) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($\times 10^5$)			Equivalents adsorbed per unit area of charcoal ($\times 10^2$)	
	HCl	NaOH	Iodine	HCl/I	NaOH/I
C_1^e	31.2 (Mean) 32.8 32.0	0 (Mean) 0 0	281 (Mean) 293 287	11.2	0
C_2^e	33.1 33.1 33.1	0 0 0	332 321 327	10.1	0
C_1	5.6 5.6 5.6	215 216 216	517 517 517	1.1	41.7
C_2	5.0 5.6 5.3	227 225 226	516 518 517	1.0	43.8
$^{\ast}C_3$	3.9 4.3 4.1	223 223 223	511 512 512	0.80	43.6
$^{\ast}C_4$	3.0 3.0 3.0	241 238 240	526 526 526	0.57	45.7
C_5	2.2 2.8 2.5	263 263 263	531 531 531	0.47	49.5
C_6	3.5 3.5 3.5	265 267 266	529 532 531	0.66	50.2
C_7	6.9 5.9 6.4	214 214 214	578 577 578	1.1	37.1
C_8	12.7 12.7 12.7	66 67 66.5	522 521 522	2.5	13.1
C_9	18.0 19.0 18.5	49 52 50.5	495 500 498	3.7	10.2
C_{10}	42.5 42.5 42.5	7.3 6.6 7.0	762 762 762	5.6	0.90

* Charcoal treated with moist air.

moisture in the air or oxygen with which charcoal is treated, promotes the formation of an alkali-adsorbing surface. As will be seen from the following considerations, however, the importance attached by the above workers to the presence of water vapour is, at least, not applicable to all cases.

After thorough evacuation at 825° charcoal A adsorbed an appreciable quantity of hydrochloric acid but no sodium hydroxide. If the evacuated charcoal (without prior exposure to the atmosphere) was then treated with carefully dried air at a temperature within the range 370°-440°, the new charcoal surface adsorbed sodium hydroxide very strongly, but practically no hydrochloric acid. Moreover the results obtained from the present investigation of the variation in the adsorption of sodium hydroxide and hydrochloric acid with temperature of treatment with dry air, are, in fact, substantially the same as those obtained by King[iv], who used moist oxygen. The similarity is most clearly demonstrated by plotting HCl/I against NaOH/I; as will be seen from Fig. 6 (page 55), the two sets of data fall approximately on a common curve.

It will be noted that in the present experiments the temperature which was found to produce maximum adsorption of sodium hydroxide and minimum adsorption of hydrochloric acid is slightly higher than that reported by King, if the NaOH/I ratios are

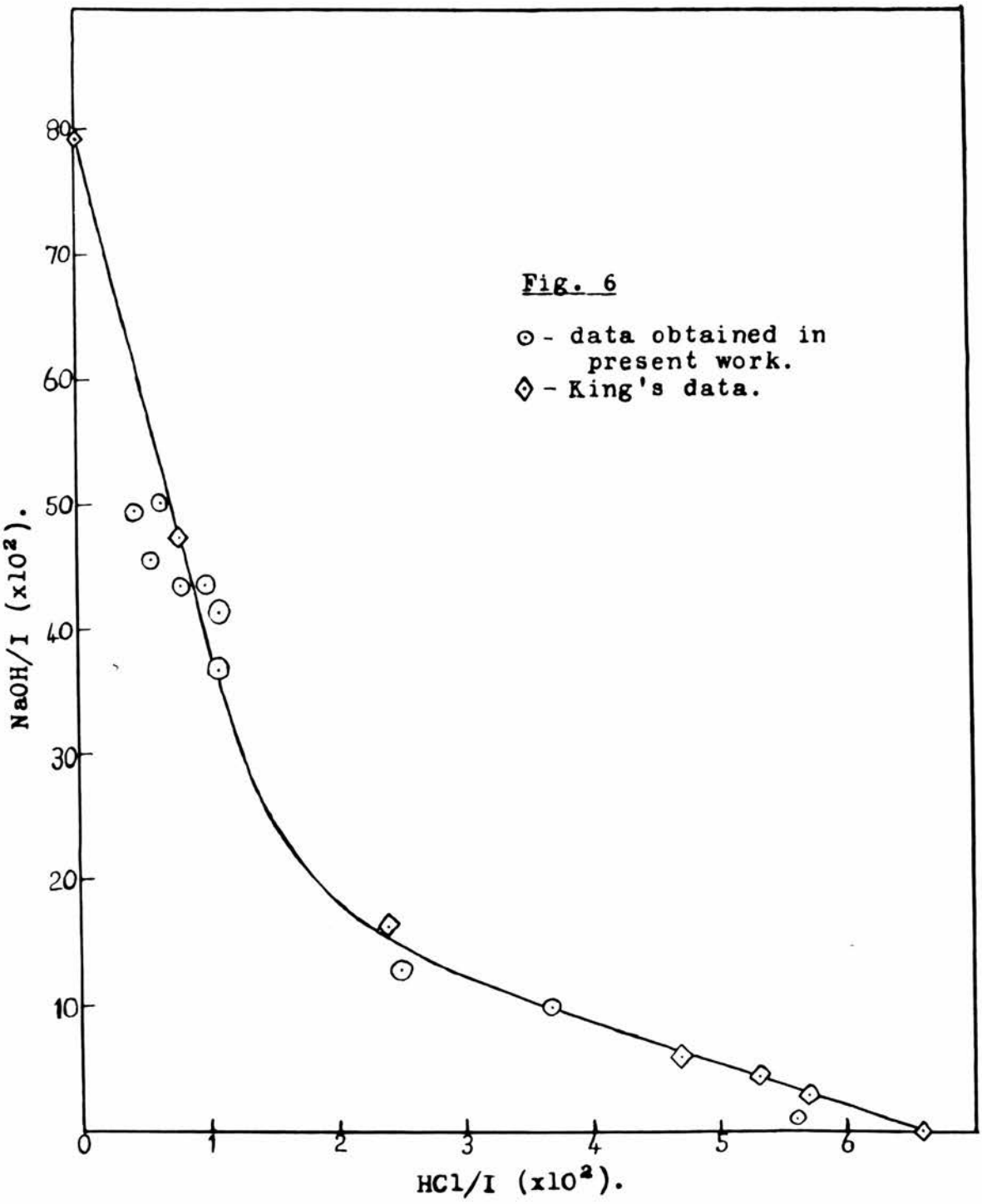

Fig. 6

⊙ - data obtained in present work.
◇ - King's data.

taken for comparison. The fact that the optimum temperature is not found to be the same by all workers is no doubt due to the varying conditions of treatment employed, but it would appear that the temperature is in the region of 400°, and not 500° as reported by Schilov[v].

It seemed possible that the favourable influence of water vapour reported by Kolthoff and Miller might be due simply to an increase in specific surface area resulting from increased combustion. The present experiments with moist air, however, show that when sugar charcoal is used, the introduction of water vapour not only has no effect upon the adsorption of sodium hydroxide, but changes neither the adsorption of iodine nor the amount of combustion.[1] This result is surprising as Kolthoff gives data showing that the presence of water vapour during treatment of charcoal increases both the adsorption of sodium hydroxide and the rate of combustion. However, it must be noted that he did not use sugar charcoal when studying the effect, and there is evidence that the degree of interaction between water vapour and charcoal depends on the source of the latter[vi]. It is still possible, therefore, that the increase in adsorption of sodium

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[1] Table II (a) shows that the overall loss resulting from treatment with dry air became practically constant above 440°, indicating that all the oxygen interacted with the charcoal. At 370°, however, the loss was much less.

hydroxide observed by him was due to increase in surface area. Kolthoff did not examine this possibility.

Effect of Treatment of Charcoal with Dry and Moist Nitrogen

On Ockrent's view, the constancy of the sodium hydroxide adsorption, irrespective of whether dry or moist air was employed in the treatment of sugar charcoal, might be regarded as due to there being made available during the air-treatment (by oxidation of hydrogen[vii] or liberation of occluded water) sufficient water to form a complete high-temperature adsorbed layer. The experiments in which samples of charcoal, after evacuation at 825°, were heated at 430° in a stream of dry nitrogen in one case, and in moist nitrogen in the other, were designed to test this possibility. As will be seen from the data in Tables III (a), (b), (c), the adsorption of alkali, very small in both cases, was actually less for moist than for dry nitrogen. This result might be considered inconclusive on the grounds that the charcoal surface, freed from water by evacuation, did not fix water when heated in the stream of moist nitrogen. It is true that Ockrent concluded that the high-temperature adsorption of water is a slow process. Actually he found that his charcoal, treated at 950° and then heated at 500° for 15 minutes in a stream of nitrogen saturated with

Effect of Treatment of Charcoal with Dry and Moist Nitrogen

Table III (a) - Treatment of Charcoal

Charcoal	Treatment	Loss in wt. (%)		Overall loss (%)
		Boat 1	Boat 2	
C_{11}	Charcoal A evacuated for 6 hrs. at 825°, then heated for 24 hrs. in dry N_2 at 430°	10.1	10.0	10.1
C_{12}	As above, but heated in moist N_2 at 430°	10.6	10.2	10.4

Table III (b) - Adsorption Data (Experimental)

Char-coal	Wt. charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 ml. HCl. (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.1N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.05N HCl.)	Wt. charcoal shaken with 25 ml. 0.1N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.05N $Na_2S_2O_3$)
C_{11}	0.3000 0.2998	0.65 0.67	0.3015 0.3008	0.17 0.18	0.3008 0.3014	8.92 8.84
C_{12}	0.3001 0.3014	0.70 0.71	0.3018 0.3003	0.06 0.07	0.3002 0.3000	9.02 9.17

Table III (c) - Adsorption Data (Derived)

Char-coal	Equivalents adsorbed per g. charcoal ($\times 10^5$)			Equivalents adsorbed per unit area of charcoal ($\times 10^2$)	
	HCl.	NaOH	Iodine	HCl/I	NaOH/I
C_{11}	28.0 28.9 28.5	7.2 7.7 7.5	361 357 359	7.9	2.1
C_{12}	30.1 30.4 30.3	2.3 3.0 2.7	365 372 369	8.2	0.72

water vapour, took up a measurable amount of water; although this was very small compared with what was desorbed on degassing charcoal, previously activated in purified air at 500°. Hence in the present instance, where the charcoal was heated at 430° for 24 hours in moist nitrogen, it is reasonable to suppose that enough water was fixed to show a very definite increase in the adsorption of alkali, if this phenomenon is really due to the fixation of water. That some water would be taken up is also indicated by the work of Strickland-Constable.[viii] The small amount of alkali-adsorption shown by C_{11} and C_{12} may well have been due to the action of oxygen present in the nitrogen since no precautions were taken to render this oxygen-free.

Effect of Heating Air-treated Charcoal in Vacuo (D-series)

Ockrent reports that when his charcoal was heated in nitrogen, the first considerable rush of desorbed water occurred at about 575°. He therefore attaches great importance to the observation made by Kolthoff that 30 hours heating at 500° did not affect the acidic surface, but heating at 575° or 600° for 24 hours reduced considerably this type of surface, as indicated by the diminished adsorption of sodium hydroxide. As a further means of testing Ockrent's hypothesis it was decided to investigate the stability of the alkali-adsorbing surface very

Degassing of Air-treated Charcoal (D-series)

Table IV (a) - Treatment of Charcoal

Char-coal	Conditions of treatment with air	Temp. and time of heating in vacuo		Vol. Air passed (l.)	Loss in wt.(%)		Overall loss(%)
		Temp.	Time(hrs.)		Boat 1	Boat 2	
D_1	Charcoal A evacuated for 6 hrs. at 825° then heated for 24 hrs. in dry air at 425°	425°	24	15.0	46.8	47.7	47.3
D_2	As above, 425°	495°	20	14.8	48.0	51.7	49.8
D_3	" " 425°	535°	24	13.5	46.8	47.9	47.4
D_4	" " 425°	520°	3	14.5	45.0	46.0	45.5
D_5	" " 440°	520°	24	13.5	47.3	46.4	46.8
D_6	" " 425°	515°	48	14.0	50.6	46.2	48.4
D_7	" " 425°	555°	48	15.0	51.6	52.8	52.2
D_8	" " 425°	750°	1	13.5	52.4	52.9	52.6
D_9	" " 430°	750°	Very short time	13.5	53.0	54.1	53.5
D_{10}	" " 430°	825°	1	15.0	64.6*	62.0	63.3

* Only the charcoal in boat 1 was used in adsorption experiments.

Table IV (b) - Adsorption Data (Experimental)

Char-coal	Wt. charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 ml. HCl. (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.1N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.05N HCl.)	Wt. charcoal shaken with 25 ml. 0.1N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.05N $Na_2S_2O_3$)
D_1	0.3018 0.3024	0.14 0.13	0.3021 0.3010	5.36 5.38	0.3010 0.3013	13.71 13.70
D_2	0.3017 0.3011	0.21 0.21	0.2996 0.3001	4.17 4.27	0.2998 0.3006	14.37 14.41
D_3	0.3015 0.3009	0.31 0.32	0.3016 0.3000	2.82 2.89	0.3015 0.3009	16.16 16.17
D_4	0.3002 0.3003	0.170 0.164	0.3008 0.2993	4.71 4.73	0.3014 0.3006	13.98 13.96
D_5	0.3001 0.3012	0.229 0.222	0.2997 0.3013	3.82 3.94	0.2993 0.3012	14.95 14.97
D_6	0.3008 0.3004	0.308 0.281	0.3013 0.3002	3.34 3.38	0.2997 0.3013	15.45 15.47
D_7	0.3003 0.3007	0.38 0.38	0.3003 0.3009	2.49 2.56	0.3021 0.3022	16.42 16.36
D_8	0.3000 0.3003	0.719 0.714	0.3002 0.3018	1.28 1.32	0.3011 0.3008	18.37 18.36
D_9	0.2998 0.3012	0.584 0.579	0.3002 0.3002	1.80 1.84	0.2999 0.3002	17.87 17.87
D_{10}	0.1954	0.681	0.2374	0.49	0.2438	17.72

Table IV (c) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($x10^5$)			Equivalents adsorbed per unit area of charcoal ($x10^2$)	
	HCl.	NaOH	Iodine	HCl/I	NaOH/I
D_1	6.0 5.6 5.8	227 229 228	554 553 554	1.1	41.2
D_2	9.1 8.9 9.0	182 178 180	583 583 583	1.5	30.9
D_3	13.4 13.8 13.6	119 124 122	655 652 653	2.1	18.6
D_4	7.4 7.1 7.3	201 202 202	564 565 565	1.3	35.7
D_5	9.9 9.6 9.8	163 168 166	607 604 606	1.6	27.3
D_6	13.3 12.8 13.1	142 144 143	627 625 626	2.0	22.9
D_7	16.5 16.4 16.5	106 109 108	661 658 660	2.5	16.3
D_8	31.2 30.9 31.1	55 56 55.5	742 742 742	4.2	7.5
D_9	25.3 25.0 25.2	77 79 78	725 724 725	3.5	10.7
D_{10}	45.3 45.3	26.2 26.2	884 884	5.4	3.0

carefully. Samples of charcoal, after treatment with dry air (425°-440°), were heated in vacuo for various periods and over a wide range of temperatures. The results of these experiments are recorded in Tables IV (a), (b), (c) (pages 60-62).

As will be seen, the results are again at variance with those of Kolthoff in that 20 hours heating in vacuo at 495° (charcoal D_2) was found actually to reduce the adsorption of sodium hydroxide by about 30%. Even 24 hours heating at the temperature at which the charcoal was treated with air produced some reduction in the adsorption of alkali (charcoal D_1). Heating for the same period at temperatures above 500° but below 575° resulted in still larger decrements in the value of the sodium hydroxide adsorption. When heating up the furnace for the experiments at 750° and 825°, desorption of gas became very rapid as the temperature increased from about 550° to 650°, and this effect may be connected with the marked decrease in sodium hydroxide adsorption referred to by Kolthoff. However, his observation that heating at 500° leaves a charcoal unaffected as regards its power to adsorb alkali is not borne out by the present experiments with sugar charcoal.[1] Ockrent's argument therefore loses its force.

It will be noted that degassing of air-treated

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[1] Kolthoff used ash-free "Nuchar" in similar experiments.

charcoal caused the value of the iodine adsorption to increase. For example the adsorption in the case of D_{10} has been increased by as much as 67% of its original value. It is difficult to see why this should happen if the surface of an "acidic" charcoal is covered simply with strongly adsorbed water which alone comes off when the temperature is raised. The desorption of oxygen as carbon monoxide and carbon dioxide and the consequent rupture of carbon-carbon bonds offers a better explanation.

Experiments with Hexaiodobenzene Charcoal

The results recorded in Tables V (a), (b), (c) on pages 65 - 66 show that the charcoal prepared from hexaiodobenzene behaved in essentially the same manner as sugar charcoal. Evacuation for 6 hours at 825° produced a charcoal (H_1^e and H_2^e) which adsorbed hydrochloric acid quite strongly, and only a small amount of sodium hydroxide. In the case of charcoal H_1^e part of the sodium hydroxide uptake was shown to be attributable to a little iodine which had not been removed during the evacuation, but this complication was found to be absent in the case of charcoal H_2^e[1].

[1] A little of the NaOH solution which had been shaken with charcoal H_1^e was acidified with conc. HCl and a few drops of starch solution added. After shaking overnight the characteristin blue colour indicating the presence of free iodine was observed. It is also worthy of note that the value 44 (for the NaOH adsorption) was obtained with a portion of the charcoal which had been ejected from the boat and therefore would be less thoroughly degassed than the remaining material which gave the smaller value 32. No iodine could be detected in NaOH solution which had been shaken with charcoal H_2^e.

Experiments with Hexaiodobenzene Charcoal

Table V (a) - Treatment of Charcoal

Charcoal	Treatment	Loss in wt. (%)
H_1^e	H_1 evacuated for 6 hrs. at 825°	15
H_1^o	H_1 evacuated for 6 hrs. at 825°, then treated with dry air for 6 hrs. at 430°	34
H_2^e	H_2 heated in a stream of purified N_2 for 6 hrs. at 825°	4.2
H_2^o	H_2 heated in a stream of purified N_2 for 6 hrs. at 825° then treated with dry O_2 for 8 hrs. at 425°	77

Table V (b) - Adsorption Data (Experimental)

Char-coal	Wt. charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 ml. HCl. (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. NaOH* (g.)	Change in titre on 10 ml. NaOH (ml. HCl)ø	Wt. charcoal shaken with 25 ml. 0.25N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.125N $Na_2S_2O_3$)
H_1^e	0.2381	1.54	0.2482 0.2470	0.62 0.85	-	-
H_1^o	0.2989	0.73	0.2447 0.2498	5.34 5.40	-	-
H_2^e	0.2001 0.1989	1.15 1.16	0.3011 0.2985	0.37 0.40	0.1981 0.1996	9.38 9.37
H_2^o	0.2094 0.2158	0.19 0.17	0.1005 0.0999	1.45 1.44	0.0899 0.0914	1.91 1.91

* 0.1N NaOH for H_1^e and H_1^o : 0.2N NaOH for H_2^e and H_2^o.

ø 0.05N HCl for H_1^e and H_1^o : 0.1N HCl for H_2^e and H_2^o.

Table V (c) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($x10^5$)			Equivalents adsorbed per unit area of charcoal ($x10^2$)	
	HCl	NaOH	Iodine	HCl/I	NaOH/I
H_1^e	84	32 44	-	-	-
H_1^o	32	280 277	-	-	-
H_2^e	75 76 76	31 35 33	1461 1448 1455	5.2	2.3
H_2^o	12 10 11	372 372 372	656 656 656	1.7	57

Evacuation at 825° followed by heating in dry air at 430°, or dry oxygen at 425°, produced a surface which adsorbed a very much larger quantity of sodium hydroxide and a markedly smaller quantity of hydrochloric acid. In the case of charcoal H_1 heating in dry air increased the adsorption of sodium hydroxide by about 900%, while in the case of charcoal H_2 the increase was even greater.

The iodine values for charcoal H_2 are peculiar in the sense that the adsorption of iodine dropped by more than 50% when an evacuated sample was activated. Activation by oxidation usually has the opposite effect. Nevertheless the values of HCl/I and NaOH/I for charcoal H_2^o are comparable with the values obtained for sugar charcoal activated under similar conditions (see Table II (c), page 53).

While it was to be expected that a large part of the small proportion of hydrogen present in the hexaiodobenzene preparations would be eliminated on charring, it still might be argued that sufficient remained to furnish charcoals H_1^o and H_2^o with a layer of high-temperature adsorbed water, to which the large alkali-adsorption should be ascribed. Hence experiments were carried out in order to ascertain the hydrogen content of charcoal H_2^e, and also that of a typical sample of sugar charcoal. The results of these experiments are recorded in Table VI on page 68.

Table VI - Hydrogen Content of Evacuated Sugar and Hexaiodobenzene Charcoals

Evacuated Sugar Charcoal (L^e)

Wt. charcoal		= 0.3138	g.
Increase in wt. of U-tube A ($1\frac{1}{2}$ hr. at 840°, N_2)		= 0.0002	g.
" " " " " " B (1 hr. " " ")		= 0.0001	g.
" " " " " " C (4 hr. " 625°, O_2)		= -0.0125	g.
" " " " " " D ($\frac{1}{2}$ hr. " " ")		= 0.0001	g.

Evacuated Hexaiodobenzene Charcoal (H_2^e)

Wt. of charcoal		= 0.2732	g.
Increase in wt. of U-tube A ($1\frac{1}{2}$ hr. at 840°, N_2)		= 0.0014	g.
" " " " " " B (1 hr. " " ")		= 0.0000	g.
" " " " " " C (4 hr. " 625°, O_2)		= 0.0058	g.
" " " " " " D ($\frac{1}{2}$ hr. " " ")		= -0.0001	g.
Wt. of residue		= 0.0011	g.
∴ Ash content		= 0.43%.	

Evacuated Hexaiodobenzene Charcoal H_1^e (after extra degassing)

Wt. of charcoal		= 0.0608	g.
Increase in wt. of U-tube A (1 hr. at 840°, N_2)		= 0.0015	g.
" " " " " " B (1 hr. " " ")		= 0.0003	g.
Vol. 0.001N $Na_2S_2O_3$ required for 15 ml. K I soln. (2 hr. at 625°, O_2)		= 6.75	ml.
" " " " " " " " " " " " "		= 0.45	ml.
" " " " " " " " " " " " " (blank)		= 0.47	ml.

(6.75 - 0.45) ml. 0.001N $Na_2S_2O_3$ ≡ 0.0008 g. Iodine.

Only the water evolved during the complete combustion (U-tube C) of each charcoal need be considered, since the water evolved in the nitrogen stream (U-tube A) was adsorbed by charcoals L^e and H_2^e at room temperature and did not impart "acidic" properties. It is at once evident that much more water was liberated by evacuated sugar charcoal than by evacuated hexaiodobenzene charcoal. Charcoal L^e gives rise to 0.0398 g. water per g. on complete combustion whereas charcoal H_2^e gives rise to only 0.0212 g. per g. Moreover, the experiment with the sample of charcoal H_1^e makes it appear doubtful if the increase in weight of U-tube C was wholly due to the absorption of water liberated in the combustion of charcoal H_2^e. Charcoal H_1^e, clearly contained occluded iodine and since there is every reason to believe that the same would be true of charcoal H_2^e, the probability is that a large part of this increase in weight of U-tube C was due to iodine adhering to the calcium chloride. Charcoal H_1^e liberated 0.0132 g. iodine per g., which is 62% of the increase in weight of U-tube C resulting from the combustion of charcoal H_2^e. The quantity of water liberated on treating charcoal H_2^e with oxygen at 425° would therefore be very much less than in the case of sugar charcoal, and yet charcoal H_2^o adsorbed, if anything, a greater amount of sodium hydroxide than a similarly treated sample of evacuated sugar charcoal. The magnitude of this

disproportionality must be regarded as indirect evidence in support of the theory that the formation of an "acidic" surface is due to combination of some kind between oxygen and carbon atoms and not to the high-temperature adsorption of water.

The experiments with hexaiodobenzene charcoal are of interest in connection with a suggestion made in a paper by Bruns, Maximova and Pos[ix] that the adsorption of alkali is due to the action of an acidic complex formed by oxidation of incompletely charred hydrogenous material present in the charcoal. These workers also point out that the best test of this hypothesis would be provided by experiments with charcoal prepared from a hydrogen-free source. As far as can be ascertained from the literature, the present experiments represent the only attempt in this direction. It was not found possible to eliminate hydrogen altogether, but the theory of Bruns, Maximova and Pos, like that of Ockrent, would lead one to expect the existence of at least approximately direct proportionality between the hydrogen content of charcoal and its capacity for adsorbing alkali after treatment with air, or oxygen. As has already been pointed out, such a relationship does not in fact hold.

Conclusion

All the evidence from the experiments so far described is against Ockrent's theory. The results

of these experiments may be summarised briefly as follows:

(1) Adsorption of alkali by sugar charcoal is not promoted by the presence of moisture in the air, or oxygen, in which the charcoal is heated.

(2) Water adsorbed at 430° by evacuated charcoal does not induce alkali-adsorption.

(3) Adsorption of alkali is decreased by heating at temperatures well below that at which, according to Ockrent, high-temperature adsorbed water, responsible for the up-take of alkali, is desorbed.

(4) Charcoal (prepared from hexaiodobenzene) containing far less water than an equal weight of sugar charcoal adsorbs alkali to the same extent as the latter.

There remains Ockrent's direct argument, namely, that he could account for the weight of a sample of sugar charcoal wholly in terms of water and carbon. In the course of the second part of the present investigation determinations were made of the amounts of water evolved on heating "acidic" charcoals under a variety of conditions. The results proved to be quite different from those of Ockrent. Moreover, strong positive evidence was obtained in favour of the usual view that the adsorption of alkali is due to the presence of chemisorbed oxygen.

In view of all these considerations it is concluded that Ockrent's hypothesis is untenable.

PART II - THE ROLE of CHEMISORBED OXYGEN

EXPERIMENTAL

Determination of Adsorption Isotherms

(a) Iodine.

An activated charcoal which it was known would adsorb iodine fairly strongly was prepared from charcoal B. Portions (0.2 g.) of this activated charcoal were weighed into six numbered pyrex tubes and iodine solutions of progressively diminishing concentration then introduced. The range of iodine concentrations was obtained in the following way.

To tube	No.	1	were added	25	ml.	Iodine (0.25N)	+	0	ml.	water.
"	"	2	"	20	"	"	+	5	"	"
"	"	3	"	15	"	"	+	10	"	"
"	"	4	"	10	"	"	+	15	"	"
"	"	5	"	5	"	"	+	20	"	"
"	"	6	"	3	"	"	+	22	"	"

After shaking for 24 hours in the usual way, the charcoal was separated from the iodine solution by centrifuging and the change in concentration determined. The results are given in Table VII (page 84). By plotting the adsorption per g. of charcoal against the equilibrium concentration the curve shown in Fig. 8a (page 104) was obtained.

(b) Sodium Hydroxide.

In order to obtain a specimen which would adsorb sodium hydroxide very strongly, a sample of charcoal B was evacuated and treated in dry air at 400° for 24 hours.

In one series of experiments portions (0.2 g.) of this charcoal were weighed into six pyrex tubes and sodium hydroxide solutions of progressively diminishing concentration (prepared in the same way as for the above iodine experiments, except that a total volume of 30 ml. solution was used), then introduced. The maximum initial concentration of sodium hydroxide solution employed in these experiments was 0.1N.

A second series of similar experiments were carried out covering a much wider range of concentrations. The results of both series are given in Table VIII and plotted in Fig. 8b.

Preparation of Oxidised Charcoal[1]

In order to facilitate the preparation of larger quantities of oxidised charcoal, the method was modified as follows. In the first place, the evacuation and oxidation of sugar charcoal were made separate operations. Charcoal B (30 g.), contained in 5 silica boats was evacuated, in the manner already described, for 6 hours at 825°. After cooling in vacuo overnight, the evacuated charcoal was removed from the furnace and stored in a bottle, closed with a rubber stopper. Several large scale evacuations were carried out and a stock of evacuated

[1] Charcoal which has been treated with air or oxygen at temperatures in the neighbourhood of 400° will now be referred to as "oxidised charcoal".

charcoal obtained. In the second place, oxygen was used for the oxidation, instead of air, so that larger quantities of charcoal could be oxidised in one operation.

The method of oxygen-treatment employed was as follows. The furnace was heated up and controlled at about 400°, the furnace tube filled with dry oxygen and the gas streamed through the apparatus at about 5 ml. per min.[1] Approximately 12 g. evacuated charcoal (contained in 2 silica boats) was then introduced and the slow stream of oxygen passed for 12 hours in each direction. After treatment the charcoal was removed, allowed to cool in a desiccator and weighed. Meanwhile another batch of evacuated charcoal (12 g.) was placed in the furnace and the passage of oxygen continued. When a stock (20-30 g.) of oxidised charcoal had been accumulated, the charcoal was returned to the furnace and treated again with oxygen at 400°. In the case of charcoals J^{o} and L^{o} the total quantity of charcoal (contained in 5 silica boats) was retreated with oxygen, at the rate of about 20 ml. per min. for 5 hours (2½ hours in each direction). In the case of charcoals K^{o} and M^{o}, separate portions of the charcoal (contained in 2 boats) were retreated with oxygen for 24 hours (12 hours in each direction) and then mixed.

Charcoals K^{o} and M^{o} were prepared using an

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[1] The rate of flow was reduced to this value to obviate excessive loss of charcoal by combustion.

improvised gas-heated furnace and a silica tube, closed at each end with rubber stoppers. The temperature could be maintained fairly constant at 400° after the initial adjustment had been made and the greatest fluctuations observed were of the order ±20°. For long periods, however, the temperature was maintained constant within much narrower limits.

Degassing of Oxidised Charcoal (J- and K-series)

The degassing experiments described in Part I provided results which suggested that it would be worthwhile carrying out further experiments under slightly different conditions. By degassing weighed samples of oxidised charcoal in a stream of purified nitrogen, the resulting loss in weight could be measured, and the period of heating could be more strictly defined than was possible when a vacuum had to be broken before the charcoal could be removed from the furnace. It was also considered important to ascertain if the amount of sodium hydroxide adsorbed by oxidised charcoal could be reduced progressively by varying the time of heating in nitrogen at a constant temperature. Actually 600° was the temperature employed.

Samples (2 g.) of oxidised charcoal (contained in a silica boat) were introduced into the furnace tube. The apparatus was evacuated, and purified nitrogen admitted slowly until the pressure was restored to atmosphere; then passed at a steady

rate of about 20-25 ml. per min., a small pulsimeter containing conc. H_2SO_4 preventing backward diffusion of air into the apparatus. The furnace was heated rapidly to about 575°; then brought to 600° cautiously, the temperature being measured by the thermocouple. About 30 minutes was required to raise the temperature to 600° and the appropriate setting of the "Sunvic" control unit maintained this temperature, with only small variations, over long periods. The furnace temperature was measured frequently during the course of each experiment; slight adjustments of the regulator setting were made when the temperature variation was appreciable, but usually this was unnecessary. The period of heating for a given sample of charcoal was measured from the moment the thermocouple indicated that the temperature had reached 600°.

Experience showed that at 600° the removal of oxygen as oxides from the surface of the charcoal was initially a rapid process, difficult to control under the above experimental conditions. For short periods of degassing, the procedure was therefore modified as follows: after filling the furnace tube with nitrogen and allowing it to stream through, the furnace was heated up and maintained at 600°; the charcoal then introduced; and the period of degassing measured from that moment. As only about a minute was required to open the exit end of the furnace tube, insert the boat containing the charcoal

and close the tube again, the admission of any significant amount of air was unlikely. Charcoal J_2 was obtained by this method, as also were charcoals K_1-K_5.

In the J- and K-series of degassing experiments the charcoal was removed from the furnace at the end of the prescribed period of heating, placed in a desiccator to cool and weighed. Purification of the nitrogen in these experiments was effected by passage over heated copper gauze (37 cm.), then through conc. H_2SO_4, and finally over phosphorus pentoxide (75 cm.).

The results of the degassing experiments with charcoals J and K are given in Tables IX(a),(b),(c) and XI(a),(b),(c), on pages 85-89.

Analysis of the Gases Evolved by Oxidised Charcoal.

Experiments somewhat similar to those described by Ockrent were carried out in order to determine the nature of the gases evolved by the oxidised charcoals. That is to say: a sample of oxidised charcoal was heated in a stream of purified nitrogen and the evolved gases absorbed in suitable reagents. The adsorptions of acid, alkali and iodine by the charcoal that remained were also measured.

The apparatus, as employed in experiments of this type, is shown in Fig. 7 (page 79). The nitrogen was freed from oxygen by passage over heated copper gauze (75 cm.), from carbon dioxide by bubbling through conc. H_2SO_4, through calcium

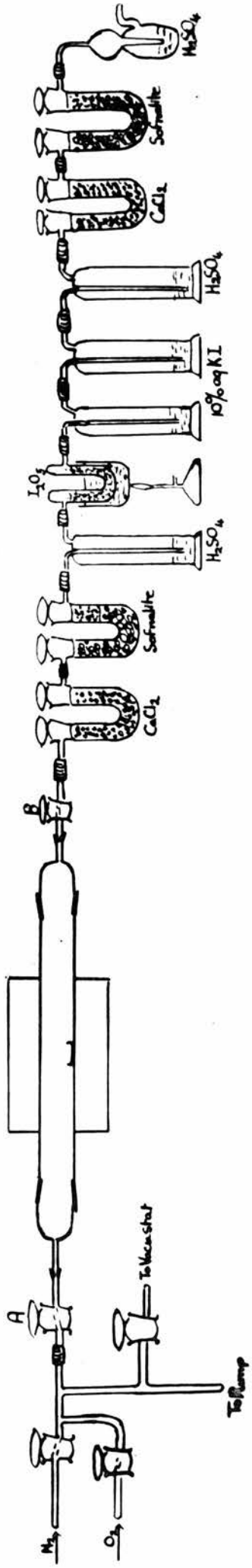
H_2SO_4
Sofnolite
$CaCl_2$
H_2SO_4
10% aq KI
I_2O_5
H_2SO_4
Sofnolite
$CaCl_2$
B
A
To Vacuostat
To Pump
H_2
O_2

Fig. 7

chloride (60 cm.) and over phosphorus pentoxide (12 cm.). It was assumed that the gases evolved would be only water, carbon dioxide and carbon monoxide. Water and carbon dioxide were adsorbed from the escaping nitrogen stream by U-tubes containing respectively calcium chloride,[1] and sofnalite and calcium chloride. The carbon monoxide was oxidised by passage through a U-tube containing iodine pentoxide, maintained at 150°, and the resulting carbon dioxide adsorbed in a second U-tube containing sofnalite and calcium chloride. The iodine evolved when the carbon monoxide is oxidised, was removed from the nitrogen stream by passage through two deschel bottles, each containing 25 ml. 10% aq. KI, and the gas subsequently dried by passage through conc. H_2SO_4 and calcium chloride[1] (one U-tube). Backward diffusion of iodine into the first sofnalite U-tube was prevented by a dreschel bottle containing conc. H_2SO_4. The small bubbler containing conc. H_2SO_4 protected the second sofnalite tube from moisture and carbon monoxide in the atmosphere.

After one or two preliminary trials the procedure adopted was as follows. Samples (2 g.) of oxidised charcoal were weighed into a silica boat and introduced into the furnace tube. The apparatus was evacuated for about 3-4 minutes and the pressure reduced to about 0.1 mm. Purified nitrogen was

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[1] The calcium chloride was rendered inert to CO_2 before use (cf. footnote (2) on page 45).

then admitted very carefully, about an hour being taken to restore the pressure to atmospheric. During this operation, the absorption U-tubes were weighed, having been previously flushed out with nitrogen. The U-tubes were connected by short pieces of thick-walled rubber tubing in the manner shown (Fig. 7, page 79) and nitrogen streamed through the entire apparatus at 20-25 ml. per min.[1]

The furnace was now heated up (rapidly at first) and controlled at the temperature at which the experiment was to be carried out. At the end of the prearranged period of heating, the furnace was switched off and a current of air blown over the outside of the furnace tube for a few minutes, in order to produce a sharp fall in temperature (about 20°).[2] The passage of nitrogen was continued, however, for a further 1-1½ hours to ensure that all evolved gases were swept out of the furnace tube and absorbed. Generally the temperature of the furnace had fallen by 200° or more in that time and the charcoal was then removed, quickly transferred to a desiccator, and weighed after 15-20 minutes. The U-tubes were disconnected, carefully wiped, and,

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[1] Before introducing charcoal into the furnace tube the precaution was always taken of displacing air from the dreschel bottles, I_2O_5 U-tube etc. by passing nitrogen direct from the cylinder for about 15 minutes.

[2] A fall in temperature of about 20° would be expected to slow down the decomposition of the surface complex(s) considerably and the further cooling effectively halt it.

after hanging beside the balance for 30 minutes, were weighed.

In order to be sure that the charcoal did not lose weight when the apparatus was evacuated, a "blank" experiment was carried out. A sample of oxidised charcoal was placed in the furnace tube and the apparatus evacuated for 5 minutes. The vacuum was broken by admitting dry nitrogen, the charcoal removed, and immediately weighed. Actually it was found to be 1 mg. heavier. The purification of the nitrogen was also tested by means of a "blank", the nitrogen being passed through the empty furnace tube at 550° for 2 hours and any resulting changes in weight of the absorption U-tubes determined.

The data obtained from these experiments are recorded in Tables XI(a),(b),(c),(d) and XII(a),(b),(c),(d) on pages 90-95.

Complete Analysis of Oxidised Charcoal

In order to determine the total amount of oxygen in an oxidised charcoal, samples of charcoal M° were analysed. The method consisted in removal of the bulk of the oxygen as oxides in a stream of nitrogen, followed by complete combustion of the degassed charcoal and determination of residual oxygen by "difference". The water, carbon dioxide and carbon monoxide were determined in the manner described above.

A weighed quantity (0.5 g.) of charcoal M°,

contained in a silica boat, was heated in purified nitrogen at about 850° for 2½ hours. The furnace was now allowed to cool for 30 minutes (nitrogen passing all the time), the stopcocks A and B then closed, the U-tubes disconnected[1] and replaced by a fresh set (flushed out with oxygen before weighing). The furnace had meanwhile cooled down to about 600°, the temperature at which it had been decided to carry out the combustion. The current was therefore switched on again and the regulator adjusted to the appropriate setting. Oxygen, freed from carbon dioxide by passage through a soda-lime tower and conc. KOH solution, and dried by passage through conc. H_2SO_4 calcium chloride (one U-tube), and finally over phosphorus pentoxide (25 cm.), was streamed through the furnace tube at 20-25 ml. per min. for 3 hours. At the end of this period the U-tubes were disconnected, carefully wiped, and weighed after an interval of 30 minutes.

A "blank" experiment was carried out in which all the operations described above were performed in the absence of charcoal. It may be noted also that during the combustion the liberation of water was actually observed; tiny droplets appeared at the exit end of the furnace tube.

The results of these analyses are presented in Table XIII on page 96.

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[1] As a "water-leak" was employed stopcocks A and B could be closed with safety during this operation.

RESULTS

Table VII - Iodine Adsorption Isotherm

Initial Concentration (N)	Equilibrium Concentration (N)	Equivalents adsorbed per g. charcoal ($x10^5$)
0.2506	0.1999	643
0.2004	0.1496	636
0.1502	0.1002	626
0.1003	0.0517	604
0.0501	0.0101	499
0.0301	0.00153	351

Table VIII - Sodium Hydroxide Adsorption Isotherm

Series I

Initial Concentration (N)	Equilibrium Concentration (N)	Equivalents adsorbed per g. charcoal ($x10^5$)
0.0959	0.0780	264
0.0799	0.0619	268
0.0640	0.0478	241
0.0480	0.0323	231
0.0320	0.0177	212
0.0160	0.00507	161

Series II

Initial Concentration (N)	Equilibrium Concentration (N)	Equivalents adsorbed per g. charcoal ($x10^5$)
0.1892	0.1675	278
0.1514	0.1303	267
0.1135	0.0931	258
0.0757	0.0556	251
0.0379	0.0209	208
0.0303	0.0143	198
0.0228	0.00816	181
0.0152	0.00354	144

Degassing of Oxidised Charcoal (J-series)

Table IX(a) - Treatment of Charcoal

Char-coal	Wt. charcoal (g.)	Treatment of Charcoal	Loss in wt. (g.)	Loss in wt. per g. charcoal (g.)
J^e	-	Charcoal B evacuated for 6 hours at 825°	-	-
J^o	-	J^e oxidised by heating in a stream of oxygen at 400°	-	-
J_1	2.000	J^o heated for 5 minutes in stream of N_2 at 600°	0.127	0.064
✱J_2	1.885	As above, 8 minutes at 600°	0.178	0.095
J_3	2.498	" " 12 " " "	0.314	0.126
J_4	2.005	" " 15 " " "	0.249	0.124
J_5	2.288	" " 21 " " "	0.423	0.185
J_6	2.001	" " 30 " " "	0.382	0.191
J_7	2.005	" " 1 hour at 600°	0.354	0.177
øJ_8	2.550	" " 6 " " 600°-610°	0.550	0.216
J_9	1.776	" " 41 " " 600°-615°	0.453	0.255
J_{10}	1.773	J^o heated up to 825° in N_2 then evacuated for 6 hrs. Vacuum broken with N_2	0.490	0.277

✱ Furnace heated to 600° before the charcoal was introduced.

ø Charcoal J_8 remained in the furnace as it cooled down for about 2 hours following a power-cut.

Table IX(b) - Adsorption Data (Experimental)

Charcoal	Wt. charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 g. HCl (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.1N HNO_3 (g.)	Change in titre on 10 ml. HNO_3 (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.2N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.1N HCl)	Wt. charcoal shaken with 25 ml. 0.25N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.125N $Na_2S_2O_3$)
J^e	0.3000 0.2997	0.59 0.60	-	-	0.3019 0.3001	0 0	0.2018 0.2020	1.40 1.37
J^o	0.5217 0.5171	0.055 0.063	0.3849	0.45	0.2992 0.2995	3.60 3.62	0.1990 0.1997	3.90 3.95
J_1	0.4332	0.119	-	-	0.3000 0.3026	2.58 2.62	0.2013 0.2001	3.76 3.66
J_2	0.3010 0.3004	0.141 0.121	0.2480	0.41	0.2518 0.2485	1.82 1.84	0.1750 0.1778	3.41 3.41
J_3	0.3509 0.3487	0.213 0.182	0.4791	0.92	0.2996 0.3006	1.77 1.84	0.2007 0.1997	4.02 4.01
J_4	0.3804 0.3655	0.220 0.194	-	-	0.3010 0.3019	1.82 1.85	0.1994 0.2014	4.01 4.01
J_5	0.3008 0.3003	0.325 0.318	0.252	0.69	0.2995 0.3015	1.10 1.11	0.2019 0.1989	4.57 4.51
J_6	0.3016 0.3016	0.321 0.326	-	-	0.2991 0.2996	1.08 1.06	0.1990 0.2010	4.61 4.70
J_7	0.3007 0.3020	0.282 0.285	-	-	0.3009 0.2986	1.20 1.21	0.2006 0.1991	4.50 4.44
J_8	0.2996 0.3003	0.598 0.597	0.3958	1.39	0.3001 0.2990	0.70 0.68	0.2011 0.1988	5.20 5.16
J_9	0.2066 0.2053	0.461 0.473	-	-	0.3005 0.3009	0.37 0.33	0.1508 0.1494	4.17 4.19
J_{10}	0.1870 0.1914	0.604 0.646	-	-	0.2978 0.2954	0.14 0.14	0.1493 0.1499	4.18 4.16

Table IX(c) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($\times 10^5$)							
	HCl		HNO_3	NaOH		Iodine	
J^e	24.6 24.2	(Mean) 24.4	-	0 0	(Mean) 0	210 206	(Mean) 208
J^o	1.3 1.5	1.4	15.3	310 312	311	595 601	598
J_1	3.4 -	3.4	-	221 222	222	568 556	562
J_2	4.9 5.7	5.3	21.6	187 191	189	592 583	588
J_3	7.5 6.4	7.0	25.0	152 158	155	608 609	609
J_4	7.1 6.5	6.8	-	156 158	157	611 605	608
J_5	13.3 13.0	13.2	35.8	95 95	95	688 689	689
J_6	13.1 13.3	13.2	-	93 91	92	704 710	707
J_7	11.5 11.6	11.6	-	101 105	103	682 678	680
J_8	24.5 24.5	24.5	45.7	60 59	60	785 786	786
J_9	27.4 28.3	27.9	-	31.7 27.9	29.8	840 851	846
J_{10}	39.7 41.2	40.5		12.1 11.8	12.0	849 842	846

Degassing of Oxidised Charcoal (K-series)

Table X(a) - Treatment of Charcoal

Charcoal*	Wt. charcoal (g.)	Treatment of Charcoal	Loss in wt. (g.)	Loss in wt. per g. charcoal (g.)
K^o	-	J^e oxidised by heating in a stream of oxygen at 400°	-	-
K_1	2.002	K^o heated for 1 hour in a stream of N_2 at 600°	0.345	0.173
K_2	2.000	As above, 6 hours at 600°	0.420	0.210
K_3	2.003	" " 42 " " 600°	0.517	0.259
K_4	2.070	" " 5½ " " 840°	0.628	0.304
K_5	2.100	" " 12 " " 840°	0.642	0.306

* In every case the furnace was heated to the required temperature before the charcoal was introduced.

Table X(b) - Adsorption Data (Experimental)

Char-coal	Wt. charcoal shaken with 25 ml. 0.1N HCl (g.)	Change in titre on 10 g. HCl (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.2N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.1N HCl)	Wt. charcoal shaken with 25 ml. 0.25N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.125N $Na_2S_2O_3$)
K^o	0.5006 0.5048	0.040 0.046	0.2019 0.2002	2.82 2.76	0.1998 0.2010	3.79 3.77
K_1	0.3205 0.3341	0.218 0.223	0.3005 0.3042	1.54 1.57	0.2025 0.2010	3.64 3.63
K_2	0.2906 0.2842	0.331 0.327	0.2986 0.3016	1.06 1.09	0.2036 0.2012	4.04 3.99
K_3	0.2546 0.2519	0.498 0.495	0.3010 0.2990	0.63 0.63	0.1893 0.1897	4.40 4.36
K_4	0.2199 0.2193	0.557 0.578	0.3000 0.3001	0.22 0.28	0.2008 0.1999	4.84 4.82
K_5	0.2277 0.2210	0.660 0.651	0.3026 0.3003	0.18 0.19	0.1994 0.2020	4.81 4.85

Table X(c) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($\times 10^5$)					
	HCl		NaOH		Iodine	
K^o	1.0 1.0	(Mean) 1.0	360 358	(Mean) 359	585 579	(Mean) 582
K_1	8.4 8.2	 8.3	132 133	 133	555 557	 556
K_2	14.0 14.1	 14.1	96 98	 97	613 612	 613
K_3	24.1 24.2	 24.2	56 57	 57	717 709	 713
K_4	31.1 32.4	 31.8	20 24	 22	744 744	 744
K_5	35.7 36.2	 36.0	16 17	 17	745 742	 744

Degassing of Oxidised Charcoal (L-series)

Table XI(a) - Treatment of Charcoal

Char-coal	Wt. charcoal (g.)	Treatment of Charcoal	Loss in wt. (g.)	Loss in wt. per g. charcoal (g.)
L_1^e	-	Charcoal B evacuated for 6 hrs. at 825°	-	-
L_2^e	-	L_1^e stored for 3 months	-	-
L_3^e	2.018	L_1^e heated for 5 hours in a stream of N_2 at 550°-560°	0.012	0.006
L_1^o	-	L_1^e oxidised in a stream of oxygen at 400°	-	-
L_2^o	-	L_1^o stored for 3 months	-	-
L_1	2.011	L_1^o heated up to 550° in a stream of N_2 and furnace switched off	0.083	0.041
L_2	1.986	L_1^o heated for 15 minutes at 550° in a stream of N_2	0.120	0.060
L_3	2.020	As above, 1½ hours at 550°	0.204	0.101
L_4	2.006	" " 3½ " " 550°	0.232	0.116
L_5	2.005	" " 1 " " 585°	0.277	0.138
L_6	1.999	" " 1½ " " 600°	0.350	0.175
L_7	2.006	" " 26 " " 600°-610°	0.421	0.210
L_8	2.003	" " 3 " " 825°	0.516	0.258

Table XI(b) - Analysis of Gases Evolved

Char-coal	Wt.H_2O evolved (g.)		Wt.CO_2 evolved (g.)		Wt.CO_2 from CO (g.)		Wt.of CO evolved (g.)	
	Found	per g. char-coal	Found	per g. char-coal	Found	per g. char-coal	Found	per g. char-coal
L_3^e	0.0063	0.0031	0.0091	0.0045	0.0108	0.0054	0.0069	0.0034
L_1	0.0140	0.0070	0.0538	0.0267	0.0392	0.0195	0.0249	0.0124
L_2	0.0167	0.0084	0.0665	0.0335	0.0815	0.0410	0.0519	0.0261
L_3	0.0161	0.0080	0.1051	0.0520	0.1644	0.0814	0.1046	0.0518
L_4	0.0193	0.0096	0.1101	0.0549	0.1885	0.0940	0.1199	0.0598
L_5	0.0147	0.0073	0.1248	0.0622	0.2006	0.1000	0.1276	0.0636
L_6	0.0130	0.0065	0.1605	0.0803	0.3037	0.1519	0.1933	0.0967
L_7	0.0105	0.0052	0.1890	0.0942	0.3811	0.1900	0.2425	0.1210
L_8	0.0191	0.0095	0.1870	0.0934	0.5091	0.2543	0.3240	0.1618
Blank	0.0001	-	0.0003	-	-0.0002	-	-	-

Table XI(c) - Adsorption Data (Experimental)

Charcoal	Wt. charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 g. HCl. (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.2N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.1N HCl)	Wt. charcoal shaken with 25 ml. 0.25N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.125N $Na_2S_2O_3$)
L_1^e	0.3023 0.3009	0.623 0.615	0.3020 0.3042	0 0	0.3058 0.3001	2.31 2.24
L_2^e	0.3071 0.3126	0.599 0.600	- -	- -	- -	- -
L_3^e	0.3844 0.3958	0.584 0.616	0.3088 0.3052	0 0	0.3018 0.3013	2.40 2.34
L_1^o	0.5781 0.5243	0.107 0.096	0.2092 0.2038	2.55 2.52	0.1994 0.1996	4.24 4.22
L_2^o	- -	- -	0.2033 0.2002	2.40 2.35	- -	- -
L_1	0.4496 0.4759	0.158 0.176	0.2998 0.3020	2.89 2.92	0.2014 0.2041	4.23 4.18
L_2	0.4209 0.4400	0.181 0.184	0.3026 -	2.65 -	0.2026 0.2017	4.20 4.15
L_3	0.4048 0.4014	0.246 0.237	0.3018 0.3065	2.07 2.08	0.1987 0.2059	4.19 4.09
L_4	0.4123 0.3624	0.327 0.272	0.3047 0.3012	1.93 1.91	0.1995 0.2010	4.39 4.40
L_5	0.3610 0.3700	0.325 0.329	0.2996 0.3006	1.62 1.62	0.2012 0.1993	4.62 4.55
L_6	0.3221 0.3215	0.446 0.458	0.3002 0.3024	1.11 1.16	0.2026 0.2008	5.05 5.01
L_7	0.3067 0.2948	0.648 0.604	0.2978 0.2963	0.56 0.56	0.1980 0.1960	5.45 5.36
L_8	0.2417 0.2517	0.800 0.833	0.3038 0.2989	0.12 0.12	0.1919 0.1927	5.84 5.87

Table XI(d) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($\times 10^5$)					
	HCl		NaOH		Iodine	
L_1^e	25.4	(Mean)	0	(Mean)	233	(Mean)
	25.2		0		230	
		25.3		0		231
L_2^e	23.9		-		-	
	23.5		-		-	
		23.7		-		-
L_3^e	18.7		0		243	
	19.2		0		237	
		19.0		0		240
L_1^o	2.3		315		656	
	2.3		319		653	
		2.3		317		655
L_2^o	-		304		-	
	-		303		-	
		-		304		-
L_1	4.3		249		632	
	4.5		249		633	
		4.4		249		633
L_2	5.3		226		632	
	5.1		-		637	
		5.2		226		635
L_3	7.5		177		634	
	7.2		175		628	
		7.4		176		631
L_4	9.7		163		671	
	9.2		163		668	
		9.5		163		670
L_5	11.2		139		700	
	11.0		139		696	
		11.1		139		698
L_6	17.0		95		760	
	17.5		99		762	
		17.3		97		761
L_7	25.9		49		840	
	25.2		49		834	
		25.6		49		837
L_8	40.6		10.2		926	
	40.6		10.4		928	
		40.6		10.3		927

Degassing of Oxidised Charcoal (M-series)

Table XII(a) - Treatment of Charcoal

Char-coal	Wt. charcoal (g.)	Treatment of Charcoal	Loss in wt. (g.)	Loss in wt. per g. charcoal (g.)
M^e	-	Charcoal B evacuated for 6 hrs. at 825°	-	-
M^o	-	M^e oxidised in a stream of oxygen at 400°	-	-
M_1	2.010	M^o heated up to 510° in a stream of N_2	0.038	0.019
M_2	2.043	M^o heated for 40 minutes in a stream of N_2 at 550°	0.176	0.086

Table XII(b) - Analysis of Gases Evolved

Char-coal	Wt. of H_2O evolved (g.)		Wt. of CO_2 evolved (g.)		Wt. of CO_2 evolved (g.)		Wt. of CO evolved (g.)	
	Found	per g. char-coal	Found	per g. char-coal	Found	per g. char-coal	Found	per g. char-coal
M_1	0.0119	0.0059	0.0278	0.0139	0.0098	0.0049	0.0062	0.0031
M_2	0.0135	0.0066	0.0968	0.0474	0.1248	0.0611	0.0794	0.0389

Table XII(c) - Adsorption Data (Experimental)

Charcoal	Wt. charcoal shaken with 25 ml. 0.1N HCl. (g.)	Change in titre on 10 g. HCl. (ml. 0.05N NaOH)	Wt. charcoal shaken with 25 ml. 0.2N NaOH (g.)	Change in titre on 10 ml. NaOH (ml. 0.1N HCl.)	Wt. charcoal shaken with 25 ml. 0.25N Iodine (g.)	Change in titre on 10 ml. Iodine (ml. 0.125N $Na_2S_2O_3$)
M^e	0.3000	0.648	0.3065	0	0.3008	2.20
	0.3013	0.643	0.3025	0	0.3008	2.14
M^o	0.6005	0.126	0.2108	2.63	0.2004	3.86
	0.6144	0.139	0.2024	2.53	0.2022	3.91
M_1	0.4796	0.129	0.3039	3.38	0.1997	3.79
	0.5003	0.136	0.3059	3.39	0.2010	3.83
M_2	0.4227	0.251	0.3000	2.20	0.2063	3.83
	0.5014	0.264	0.2990	2.20	0.2027	3.71

Table XII(d) - Adsorption Data (Derived)

Charcoal	Equivalents adsorbed per g. charcoal ($\times 10^5$)					
	HCl		NaOH		Iodine	
M^e	25.2	(Mean)	0	(Mean)	228	(Mean)
	25.2		0		222	
		25.2		0		225
M^o	2.5		313		603	
	2.7		313		601	
		2.6		313		602
M_1	3.2		279		592	
	3.2		276		594	
		3.2		278		593
M_2	7.0		184		579	
	6.3		184		572	
		6.7		184		576

Table XIII - Complete Analysis of Oxidised Charcoal (M^0)

Experiment 1.

Treatment of charcoal							
Streaming N_2 at 855° ($2\frac{1}{2}$ hrs. + $\frac{1}{2}$ hr. cooling)				Combustion in O_2 at 625° (3 hrs.)			
Wt. H_2O evolved (g.)	Wt. CO_2 evolved (g.)	Wt. CO_2 from CO (g.)	Wt. CO evolved (g.)	Wt. H_2O evolved (g.)	Wt. CO_2 evolved (g.)	Wt. CO_2 from CO (g.)	Wt. CO evolved (g.)
0.0045	0.0455	0.1463	0.0931	0.0218	0.9365	0.4191	0.2667

Sum of wts. of gases evolved in N_2 stream = 0.1431 g.

Residual carbon (from combustion data) = 0.3697 g.

Wt. of hydrogen (" " ") = 0.0024 g.

Total = 0.5152 g.

Wt. of charcoal taken = 0.523 g.

Difference = 0.008 g.

Experiment 2.

Treatment of charcoal							
Streaming N_2 at 865° ($2\frac{1}{2}$ hrs. + $\frac{1}{2}$ hr. cooling)				Combustion in O_2 at 625° (3 hrs.)			
Wt. H_2O evolved (g.)	Wt. CO_2 evolved (g.)	Wt. CO_2 from CO (g.)	Wt. CO evolved (g.)	Wt. H_2O evolved (g.)	Wt. CO_2 evolved (g.)	Wt. CO_2 from CO (g.)	Wt. CO evolved (g.)
0.0073	0.0435	0.1399	0.0891	0.0206	0.8470	0.4350	0.2768

Sum of wts. of gases evolved in N_2 stream = 0.1399 g.

Residual carbon (from combustion data) = 0.3496 g.

Wt. of hydrogen (" " ") = 0.0023 g.

Total = 0.492 g.

Wt. of charcoal taken = 0.498 g.

Difference = 0.006 g.

DISCUSSION

In Part I (page 71) it was indicated that the results of certain of the experiments described in Part II were quite different from those obtained by Ockrent[i] under comparable conditions. It will be convenient, as well as logical, to deal with this matter before proceeding to discuss other important aspects of the data.

The Evolution of Water from Oxidised Charcoal

The relevant data (see Tables XI(a) and XI(b) on pages 90 - 91) have been brought together in the following table:

Table XIV

Charcoal L	Temperature (°C.)	Period of heating	g. H_2O evolved from 1 g. charcoal ($\times 10^4$)
1	550	Very short	70
2	"	15 mins.	84
3	"	1½ hrs.	80
4	"	3½ "	96
5	585	1 hr.	73
6	600	1½ hrs.	65
7	600--610	26 "	52
8	825	3 "	95

These results differ markedly from those of Ockrent. In the first place the quantities of liberated water are much smaller than those reported in his paper (ca. 0.15 g. H_2O per g. char-

coal). Secondly the amount of water is independent of both the period of heating and the temperature employed, i.e. the bulk of the water is released on heating for a short time at the lowest temperature (550°). Moreover, visual observation suggested that all this water was evolved while the furnace temperature was rising from about 200° to about 300°. Ockrent found that only about one-quarter of the total water obtainable on degassing his charcoal, was evolved as the temperature was slowly raised to 575°. Even that smaller quantity of water is far in excess of the amounts found in this investigation, but it must be noted that Ockrent allowed his charcoal samples to stand for a considerable time exposed to the air before weighing.

As to the source of Ockrent's large quantities of water, a probable explanation is to be found in his method of preparing activated charcoal, since his crude sugar charcoal was evacuated for only 3 hours at 500° before treatment with purified air. In this investigation charcoals A and B were prepared by roasting crude sugar charcoal for 40 minutes over a Méker burner (flame temp. about 900°) and, as reported on page 12, much further decomposition of partially charred sugar took place. Samples of charcoals A and B were also evacuated at 825° for 5 hours before treatment with air or oxygen, in an attempt to ensure that charring was complete and all decomposition products removed.

It is certain that evacuation and activation at 500° would be less effective in eliminating partially charred sugar from crude charcoal. As Ockrent observed, degassing and reactivation of his charcoal A did not significantly affect the total quantity of water evolved. Consequently the large quantities of water which he obtained when the temperature was raised above 575° may well have been due to further pyrolysis and it seems anomalous that the weight of Ockrent's charcoal could be accounted for in terms of water and carbon only.

The discontinuous evolution of water from Ockrent's charcoal at definite temperatures is less easily explained. It should be noted, however, that Ockrent reports that when his crude sugar charcoal was slowly heated to 950° "large quantities of non-condensable gases and water vapour were evolved in sudden rushes". In view of this, the discontinuities in the evolution of water from Ockrent's activated charcoal also suggest that this water resulted from pyrolysis.

Whatever the explanation, it is clear from the present work that the decrease in the adsorption of alkali produced by heating the charcoal in a stream of nitrogen is not due to the removal of water from the charcoal surface. The adsorption decreases continuously with increase in the period of heating or in the temperature employed (see Tables IX-XII on pages 85-95), whereas the amount of water evolved

undergoes relatively small irregular variations.[1] For example, the loss of water in the case of charcoals L_2 and L_8 is practically the same, but L_8 adsorbs only about one-twentieth of the amount of alkali adsorbed by L_2 (see Table XI(d) on page 93). Thus these experiments appear to rule out Ockrent's idea that the adsorption of alkali is due to the presence of a special type of adsorbed water on the surface of charcoal.

The Composition of Oxidised Charcoal

Complete analysis of charcoal M^o yielded very interesting results. The following table shows the composition of the charcoal, as calculated from the data in Table XIII (page 96).

Table XV

Expt.	Weight (g.) per 100 g. charcoal					Deficiency (g.)
	H_2O[1]	O	C	H	Total	
1	0.86	16.50	80.70	0.46	98.52	1.48
2	1.47	16.58	80.25	0.46	98.76	1.24

In these calculations it is assumed that all the water was evolved during the heating in nitrogen prior to the combustion, and, therefore, that the water obtained in the combustion was derived wholly from hydrogen present as such or in the form of

[1] See page 109 re variation of water-content.

organic compounds.[1] The oxygen was that present as CO_2 and CO found in the nitrogen stream, while the carbon figure represents the sum of the quantities present in these gases and that found (by combustion) in the residual charcoal. The small deficiency of less than 1.5% probably means that the residual charcoal contained a little oxygen in the form of water,[2] or fixed by the charcoal and evolved as CO and CO_2 on combustion, or present in the elementary state and evolved in the nitrogen stream (or on combustion). In any case the figures for water and oxygen would be affected to only a minor extent if the appropriate corrections were made.

The results are completely at variance with Ockrent's conclusion that charcoal after heating in air consists exclusively of carbon and water, and therefore cannot contain any oxygen fixed on its surface. Table XV shows that at least 16.5% of the weight of charcoal M^o must be allotted to fixed oxygen. This disposes of Ockrent's main argument, namely, the lack of oxygen in the charcoal, in support of his theory that the adsorption of alkali must be due to adsorbed water, and not to surface

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[1] Ockrent assumes that the water he obtained on combustion of his charcoal was present as such. A fraction of the water adsorbed by charcoal has been reported as held irreversibly,[x] but Lawson[xi] has shown that this is not the case if an ash-free charcoal is used.

[2] The assumption that the whole of the hydrogen was present as water gives too high a value for the total weight.

oxides.

It is possible that Ockrent's charcoal did actually contain a very small proportion of fixed oxygen, as he reports that small quantities of carbon dioxide were found in the nitrogen stream. He includes their carbon in his carbon figure, but they may well have been indicative of the presence of fixed oxygen. That the amount of fixed oxygen would be small is understandable, since a large mass (109 g.) of charcoal was activated for only 2 hours, and in a very rapid stream of air, conditions unfavourable to fixation.[1]

Finally it should be emphasised that Ockrent does not give any figures for the adsorption of alkali. Hence it remains uncertain to what degree his charcoals were capable of such adsorption. The present investigation has shown that treatment of sugar charcoal with air at 500° results in only a fraction of the maximum sodium hydroxide adsorption, obtained with charcoal oxidised at about 400°. In view of this and also of the positive evidence (see later) that the adsorption depends upon the presence of fixed oxygen, it is probable that Ockrent's material did in fact adsorb only very little alkali.

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[1] Kolthoff[ii] reports that the "initial formation of the acid takes place slowly, but once started progresses rapidly".

Adsorption of Iodine

It was observed that 25 ml. 0.1N iodine solution was almost completely decolourised by 0.3 g. of the highly active charcoals (C_{10}, D_8, D_9, D_{10}). A solution of higher concentration (0.25N) was therefore prepared, and the adsorption isotherm determined. The results obtained (see Table VII on page 84 , and Fig. 8a on page 104) show that the iodine adsorption does not differ significantly from the saturation value until the equilibrium concentration is less than 0.15N. Charcoal H_2^e (0.2 g.) reduced the equilibrium concentration a little below 0.15N, but in the case of all other charcoals the equilibrium concentration was well above that figure when 0.25N iodine was employed. The iodine adsorptions in Part II are therefore saturation values.

Adsorption of Alkali

Since in this work the adsorption of sodium hydroxide is taken as a measure of the amount of acidic complex(s) on the surface of oxidised charcoal, it was essential to employ a stock solution of such a concentration that no significant variation in the adsorption with change in the equilibrium concentration should take place. The adsorption isotherm was therefore determined.

The results (see Table VIII on page 84 , and Fig. 8b on page104) show that over a considerable range of concentrations, the adsorption of sodium

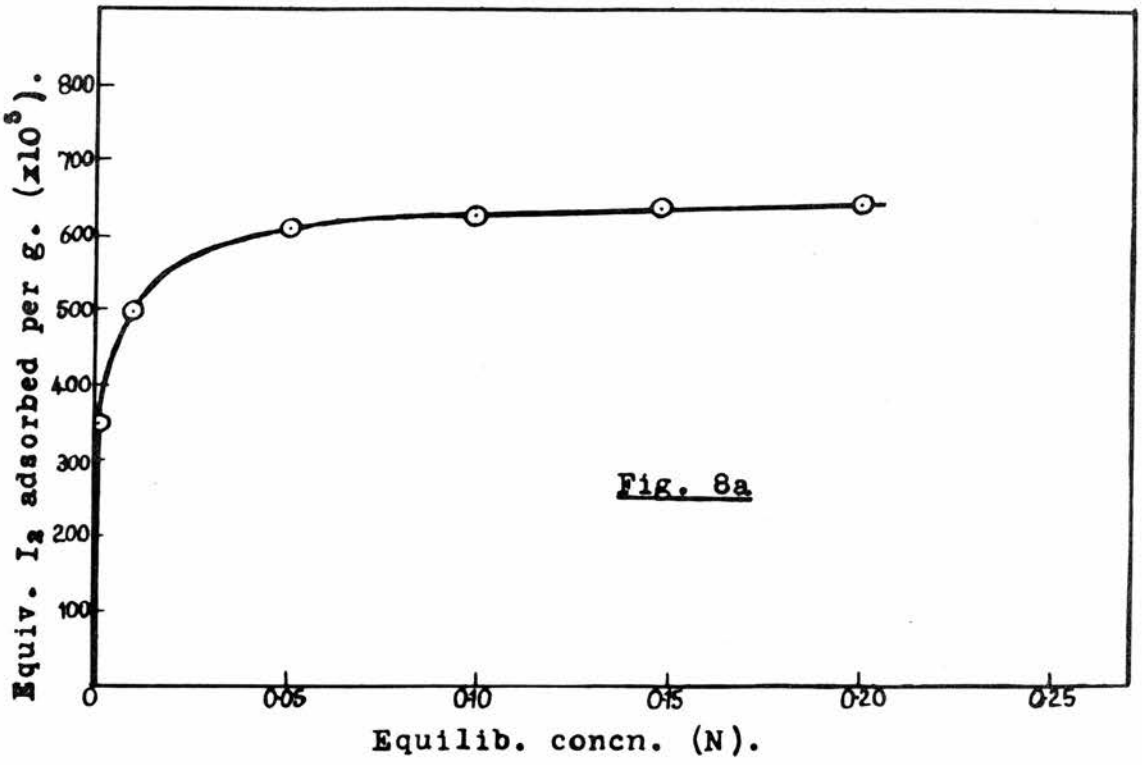
Equiv. I_2 adsorbed per g. ($\times 10^5$).
800
700
600
500
400
300
200
100
0
0·05
0·10
0·15
0·20
0·25
Equilib. concn. (N).

Fig. 8a

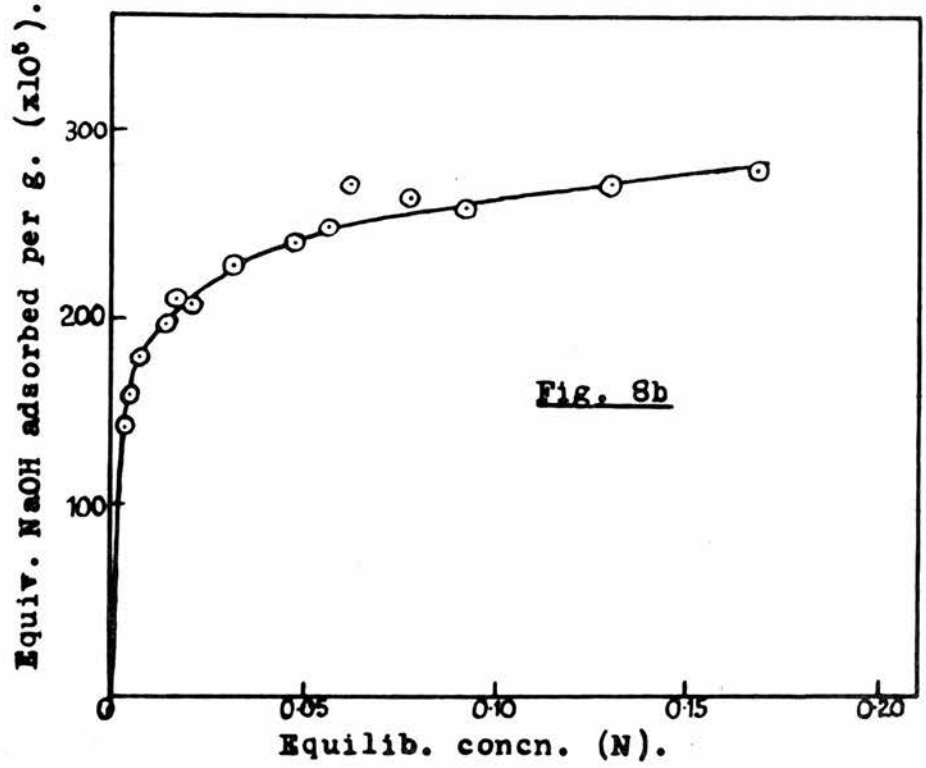
Equiv. NaOH adsorbed per g. ($\times 10^6$).
300
200
100
0
0·05
0·10
0·15
0·20
Equilib. concn. (N).

Fig. 8b

hydroxide does vary with the equilibrium concentration, a curve resembling the familiar parabolic curve being obtained when these quantities are plotted. The adsorption of sodium hydroxide is noticeably less than the saturation value when the equilibrium concentration falls below 0.1N. Consequently, when a solution of initial concentration 0.1N was used, the sodium hydroxide adsorptions were somewhat low and this error would be greatest in the case of the strongly acidic charcoals (e.g. C_5 and C_6). In Part II, however, all the sodium hydroxide adsorptions were measured using 0.2N solution and the equilibrium concentration was always greater than 0.15N. Thus the complications referred to above do not arise.

These experiments agree with those of Weller and Young[xii] whose work was published while this investigation was in progress. Weller and Young also observed that the adsorption of alkali depended quite markedly on the time of contact of the charcoal and solution. About 20 hours was required before the adsorption reached its maximum value, although this period could be reduced by grinding the charcoal. These facts were not taken into account by Strickland-Constable[xiii] when he attempted to relate the oxygen content of one of his charcoals to its capacity for adsorbing alkali. Strickland-Constable determined the adsorption of sodium hydroxide by shaking 0.5 g. of charcoal with

25 ml. 0.02N alkali for half-an-hour and under these conditions the adsorption of sodium hydroxide would amount to but a small fraction of its saturation value. His conclusion that the oxygen with acidic properties is only a small proportion of the total oxygen on the surface of oxidised charcoal is therefore not justified.

The relative adsorptions of lithium, sodium and potassium hydroxides from 0.2N solution were also determined. The results obtained with a typical sample of oxidised charcoal are given below:

Equivalents LiOH adsorbed per g. charcoal = 395×10^{-5}

" NaOH " " " " = 348×10^{-5}

" KOH " " " " = 335×10^{-5}

While the adsorptions of these three bases are of the same order of magnitude, the differences are outside the limits of experimental error and therefore must be real. At present it does not seem possible to offer a reasonable interpretation of these figures.

The Loss in Weight on Degassing Oxidised Charcoal

When oxidised charcoal was heated in nitrogen, it was found that the observed loss in weight was consistently less than the sum of the weights of water, carbon dioxide and carbon monoxide evolved (see Table XI(b), on page 91). However, the loss in weight was a somewhat uncertain quantity since, after removal from the furnace, the charcoal gained weight (even on standing in the desiccator) and for that reason the weighings were always carried out after a constant interval (15-20 minutes). It seems reasonable to suppose that this increase in weight of the charcoal is due to re-adsorption of water vapour, as the relative humidity of the atmosphere in the laboratory was high after these experiments.[1] Consequently, if water vapour is taken up again rapidly, the observed loss in weight will be less than expected.

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[1] The gas burners used to heat the copper gauze over which the nitrogen passed, gave off large quantities of water vapour into the atmosphere.

Table XVI*

Charcoal	Loss in wt. (observed) (g.)	Wt. CO_2 + Wt. CO (g.)	Difference (g.)
L 1	0.083	0.0787	-0.004
2	0.120	0.1184	-0.002
3	0.204	0.2097	+0.006
4	0.232	0.2300	-0.002
5	0.277	(0.2524)ø	-
6	0.350	0.3538	+0.004
7	0.421	0.4315	+0.011
8	0.516	0.5110	-0.005
M 1	0.038	0.0340	-0.004
2	0.176	0.1762	0.000

When the loss in weight is compared with the sum of the weights of carbon dioxide and carbon monoxide alone (see Table XVI), it will be noticed that the differences are quite small and variable in sign. This result suggests that after removal from the furnace, the charcoal re-adsorbs about as much water as was present on the surface of the charcoal before heating in nitrogen. The actual quantity taken up will depend on a number of factors (humidity, time of exposure to the air and the nature of the charcoal surface) and therefore must

* From data in Tables XI(a),(b) and XII(a),(b).

ø Some gas was lost when the pressure inside the furnace tube forced out the ground end momentarily during the early stages of the degassing.

be expected to vary from experiment to experiment. In some cases more water may be adsorbed than was lost, and in others less. The variations in the magnitude and sign of the difference between the sum of the weights of carbon dioxide and carbon monoxide and the observed loss in weight are explained in this way.

An experiment was carried out to test this interpretation. A sample of charcoal M^{o} (2 g.) was degassed at 585^{o} for 30 minutes and the evolved water weighed. After keeping in the desiccator for 15 minutes, the charcoal was quickly transferred to the furnace and heated at 585^{o} for a further 30 minutes in streaming nitrogen, the emergent gas being passed through a fresh U-tube containing calcium chloride. During the first treatment at 585^{o} 0.0176 g. water was evolved and after the second treatment 0.0130 g. water was collected. Since precautions were taken to prevent diffusion of water vapour from the atmosphere into the furnace tube while it was unsealed, the second quantity of water must have come from the charcoal. Hence in this experiment 70% of the water evolved during the first degassing was re-adsorbed by the charcoal when it was removed from the furnace and exposed to the air.

It is now clear why the weight of water evolved by samples of the same batch of oxidised charcoal shows irregular variations. The time taken to

weigh out 2 g. of charcoal into the silica boat and transfer it to the furnace tube would not be the same in each experiment. Consequently variable amounts of water vapour would be taken up by the charcoal while it was exposed to the air. This is well illustrated in the case of Expts. 1 and 2, Table XIII (page 96). The portion of charcoal used in Expt. 1 was placed in the furnace tube immediately after weighing, whereas the charcoal used in Expt. 2 was kept in the desiccator for 15 minutes and then weighed again before being placed in the furnace tube. The second weighing showed an increase in weight of 4 mg. and it will be noted that the weight of water evolved by the charcoal in Expt. 2 is 7.3 mg. as compared with 4.5 mg. in Expt. 1.

Products of Degassing.

The data in Table XVII (page 111) are derived from the experimental results recorded in Tables XI(b), XII(b), XIII on pages 91 - 96. If the observed loss in weight is plotted against the total amounts of oxygen and carbon lost, it is found that straight-line relationships hold throughout the greater part of the degassing (see Fig. 9 on page 112). These straight lines indicate that within the limits concerned, carbon dioxide and carbon monoxide are evolved in fixed proportions. It should be noted that the loss in weight for charcoal

L_8 is slightly high, owing to incomplete re-adsorption of water (see Table XVI). The points for M^o are regarded as fixing the change in slope of the curves (at high losses), since in their case the loss is calculated from the weights of carbon dioxide and carbon monoxide.

Figure 10 (page 113) shows the variation in the proportions of oxygen as carbon dioxide and as carbon monoxide with increase in the total oxygen evolved.

Table XVII

Charcoal	Loss in wt. (%)	Moles oxygen evolved per g. charcoal ($x10^5$)			Total g. atoms carbon in CO_2 and CO from 1 g. charcoal ($x10^5$)
		As CO_2	As CO	Total	
L 1	4.1	61	23	84	105
2	6.0	76	47	123	170
3	10.1	118	93	211	305
4	11.6	125	108	233	337
5	13.8	(148)	(133)	(282)*	(412)**
6	17.5	182	173	355	528
7	21.0	214	216	430	646
8	25.8	212	289	501	791
M 1	1.9	31.4	5.6	37	42.5
2	8.6	108	69	177	247
ø(Expt.1)	§(26.5)	198	318	516	833
ø(Expt.2)	§(26.6)	199	319	518	837

* From - loss in weight/loss of oxygen curve (Fig. 9, page 112).

** From - loss in weight/loss of carbon curve (Fig. 9, page 112).

ø From Table XIII (heating in N_2 stream).

§ Sum of weights of CO_2 and CO evolved by 1 g. of charcoal.

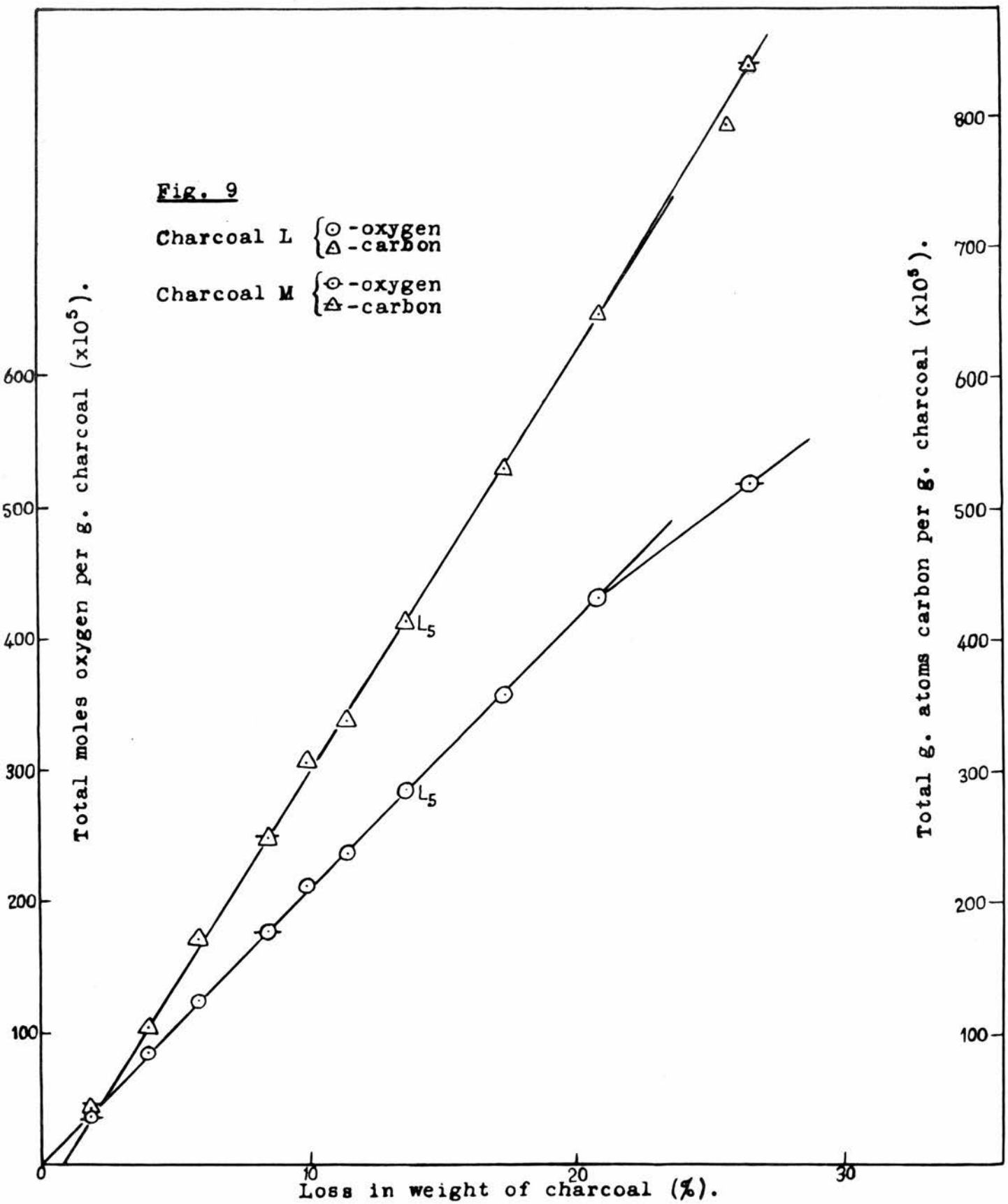
Fig. 9
Charcoal L ⊙-oxygen △-carbon
Charcoal M ⊙-oxygen △-carbon
Total moles oxygen per g. charcoal (x10⁵).
Total g. atoms carbon per g. charcoal (x10⁵).
Loss in weight of charcoal (%).
L5
L5
0
10
20
30
100
200
300
400
500
600
700
800

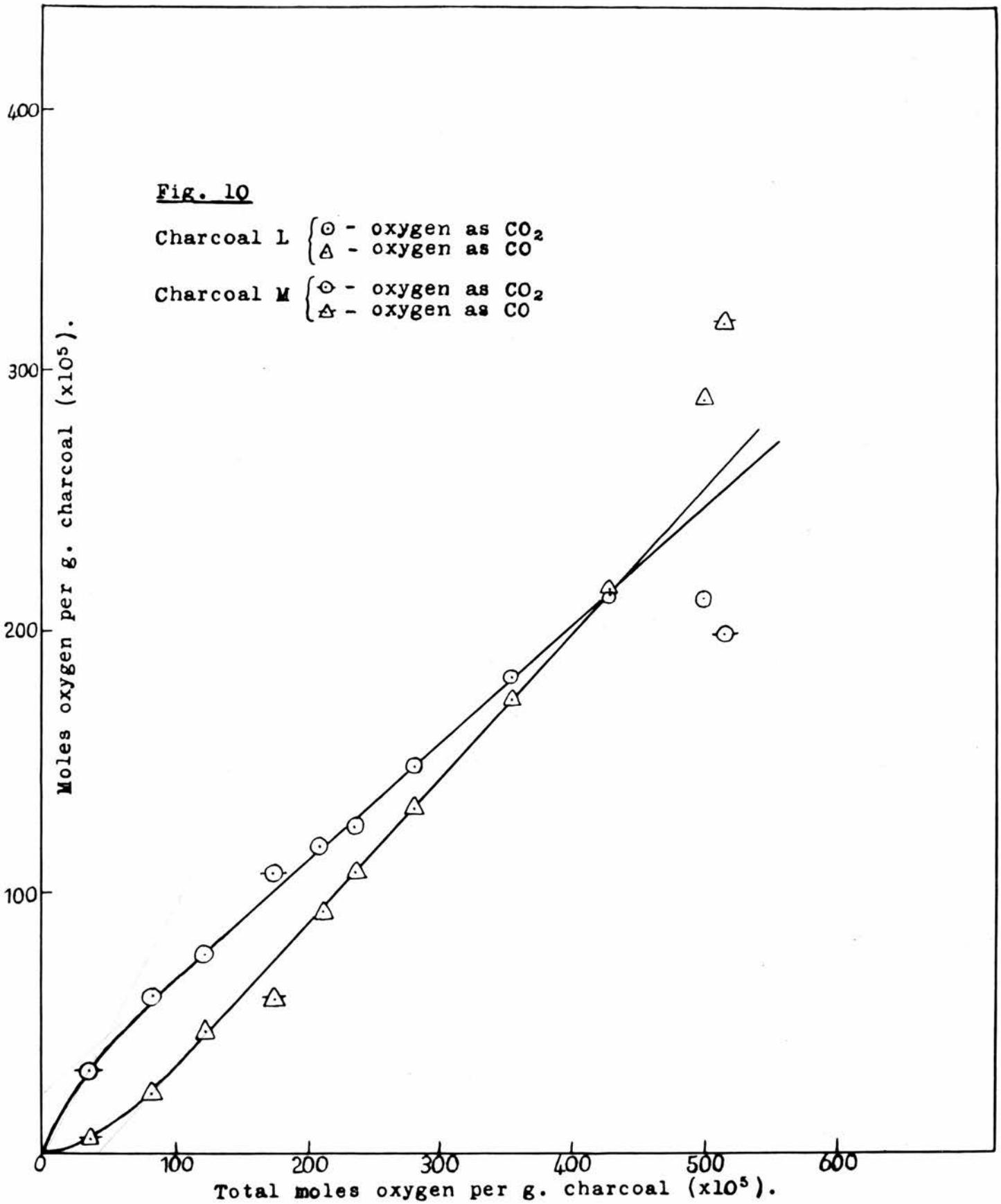
Fig. 10
Charcoal L ⊙ - oxygen as CO_2
△ - oxygen as CO
Charcoal M ⊙ - oxygen as CO_2
△ - oxygen as CO
Moles oxygen per g. charcoal (x10⁵).
Total moles oxygen per g. charcoal (x10⁵).
0
100
200
300
400
500
600

It will be seen that practically carbon dioxide alone is formed when the loss is very low, and that the slopes of the curves become constant at a total oxygen value of about 80 moles ($x10^5$). The change in gradient of the curves (at high losses) may be attributed to reduction of carbon dioxide to carbon monoxide at the charcoal surface, leading to removal of extra carbon atoms. The large losses were obtained after prolonged heating at 600°, or by heating for shorter periods at over 800°, and under these conditions some interaction of the carbon dioxide evolved and the charcoal would certainly be expected. This complication apparently does not arise when the charcoal is heated for shorter periods at 600°, but it has been noted (see page 77) that at 600° the degassing proceeds very rapidly at first, and it is conceivable that the carbon dioxide is removed too quickly from the neighbourhood of the charcoal for reduction to take place.

Although charcoals L^o and M^o were obtained from the same stock of crude sugar charcoal, they are nevertheless quite separate preparations (see page 75). Clearly the oxygen is evolved in substantially the same way by each of these charcoals. Figures 9 and 10 therefore have general application and when only the loss in weight is known, as in the case of charcoal L_5 and in the J- and K-series of experiments, the graphs can be used to estimate the amount of total oxygen, oxygen as carbon dioxide and

oxygen as carbon monoxide evolved at any given stage. The experimental values for charcoal L_5 given in Table XI(b) (page 91) are incorrect, owing to an escape of gas, and the values given in Table XVII were obtained from Figs. 9 and 10.

It is interesting to note that the oxygen contents (calculated from the carbon dioxide and carbon monoxide evolved in the nitrogen stream at 850°) of charcoals L^o and M^o (501 and 517 x 10^{-5} moles per g.) are only a little less than the maximum value (18.3% O_2 by weight of charcoal, i.e. 572 x 10^{-5} moles per g.) reported by Weller and Young.[xii] Furthermore, it is necessary to point out that Weller and Young consider all the water obtained in the combustion of their charcoals as coming from hydrogen present as such. These workers overlook the fact that a portion of the water evolved would simply be that which was adsorbed on the surface. If it is assumed that their highly oxidised charcoal (TUC-46) contained an amount of water comparable with the quantities found in the present investigation, then their "fixed oxygen" content would be reduced by 0.5-1.0%. The values found in this work can also be raised to nearly 18% by including the "differences" obtained in the analysis experiments (see Table XIII on page 96).[1] In highly oxidised charcoal, therefore, it is

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[1] See, however, page 125.

possible to have a proportion of approximately one oxygen molecule to every six carbon atoms. Moreover, the high loss in weight (30%) resulting when charcoal K° was degassed at 840° indicates that an even lower proportion of carbon atoms may be attained.

These results are in marked contrast to those of Strickland-Constable,[xiii] who obtained only 25 c.c. of oxygen (as oxides) per g. from a charcoal which had been treated with nitrous oxide at 403° and was considered to be "largely saturated with surface oxides". This small volume of oxygen (equivalent to about 112 x 10^{-5} moles) led Strickland-Constable to conclude that the idea of a carbon surface completely covered with sorbed oxygen atoms is fallacious, and that, in fact, only a very few points on the surface of charcoal are available at any one time for attachment of oxygen. However, the present investigation and that of Weller and Young, have shown that very much higher oxygen contents can be built up, although as Emmett[xiv] points out, these correspond to no more than about a monolayer of oxygen on the surface of charcoal.

Relatively small oxygen contents are also reported by Rhead and Wheeler,[xv] and Shah.[xvi] Rhead and Wheeler heated a quantity of charcoal (9.7 g.) at 300° in a slow stream of dry air for 6 hours and considered fixation of oxygen to have ceased at the end of that period. On degassing

(the temperature being raised stepwise to 1000°) 79 c.c. of oxygen (as oxides) were obtained, corresponding to only about 35×10^{-5} moles oxygen per g. On the other hand Shah's charcoal (5 g.) was alternately treated with charges (30 c.c.) of nitrous oxide and exhausted at 470°. After the tenth treatment the charcoal was degassed (the temperature being increased stepwise to 950°) and 16.1 c.c. of carbon dioxide and 51.3 c.c. of carbon monoxide were evolved; these volumes are equivalent to no more than about 40×10^{-5} moles oxygen per g. But the temperatures of treatment of charcoal in the above cases are significantly different from the optimum temperature for fixation of oxygen observed in this investigation.

Reference was made on page 114 to the fact that when oxidised charcoal L° is degassed, initially the main product is carbon dioxide, but that after 80×10^{-5} moles oxygen per g. has been lost, the ratio of carbon dioxide to carbon monoxide becomes constant. This initial preponderance of carbon dioxide in the evolved gases has been observed by the above mentioned workers,[1] but they also report that the amount of carbon dioxide evolved per increment of temperature becomes progressively less, until finally almost pure carbon monoxide is evolved. In this respect, therefore, the present data appear to be unique.

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[1] Rhead and Wheeler, Shah and Strickland-Constable.

Relationship between the Loss of Fixed Oxygen and the Decrease in the Sorption of Sodium Hydroxide

From a thorough search of the literature it would appear that hitherto no systematic quantitative investigation has been made of the sorption of base and the fixation of oxygen by one and the same charcoal.

In columns 2 and 3 of Table XVIII (page 120) the decreases in the sorption of sodium hydroxide and the quantities of oxygen evolved (as oxides) are recorded; the oxygen-losses for charcoals J and K are the values derived from Figs. 9 and 10 (pages 112-113). The method of calculating the decreases in sodium hydroxide sorption requires a note of explanation. Suppose, for example, that 1 g. of oxidised charcoal sorbs 300×10^{-5} equivalents of alkali, that after heating in nitrogen there is a loss in weight of 0.2 g., and that the new sorption of alkali is 200×10^{-5} equivalents per g. The actual loss of alkali-sorption is therefore 140×10^{-5} equivalents ($300-0.8 \times 200$). This method of calculation refers all the changes in the sorption of sodium hydroxide to the original 1 g. of oxidised charcoal.

When the oxygen losses are plotted against the decreases in the sorption of sodium hydroxide (see Fig. 11, curve I, on page 121), the graph obtained provides striking evidence of the existence of a definite relationship between the amount of chemi-

sorbed oxygen on the surface of charcoal and its capacity for sorbing alkali. All the L-points lie on, or within ±3% of, a smooth curve. The number of atoms oxygen evolved for unit loss of sodium hydroxide sorbing power increases continuously until about 550-600 atoms oxygen have been lost; but then becomes constant, the points lying on a straight line. Examination of curve I reveals that in the region of strict proportionality, the best straight line through the points has a gradient of exactly $\frac{1}{4}$, but that in the region of low oxygen-losses the gradient tends to $\frac{1}{2}$. Initially, therefore, 1 molecule of sodium hydroxide is equivalent to 2 atoms oxygen and finally, to 4 atoms oxygen.

If one postulates that two types of oxygen-complex, α and β, are involved in the sorption of base, such that the ratio of atoms oxygen to molecules sodium hydroxide is 2:1 in the case of α and 4:1 in the case of β, the shape of the curve is readily explained. The total sorption of sodium hydroxide has to be shared between these two complexes and the actual distribution may be simply calculated by the solution of two simultaneous equations; thus:

Let x = the NaOH adsorption due to α,

and " y = " " " " " β.

It follows that: $2x + 4y$ = total oxygen evolved,

and: $x + y$ = total decrease in NaOH adsorption.

Table XVIII

Char-coal	Decrease in NaOH sorbed by 1 g. charcoal equivalents ($\times 10^5$)	Total oxygen evolved per g. charcoal g. atoms ($\times 10^5$)	NaOH-sorption due to complex α equivalents ($\times 10^5$)	NaOH-sorption due to complex β equivalents ($\times 10^5$)
✱L_1	72	168	60	12
2	98	246	73	25
3	154	422	97	57
4	164	466	95	69
5	190	(564)	(98)	(92)
6	230	710	105	125
7	272	860	114	158
8	303	1002	105	198
M_1	33	74	29	4
2	142	354	107	35
Expt. 1	(313)ø	1032	110	203
Expt. 2	(313)ø	1036	108	205
J_1	104	(260)	-	-
2	140	(384)	-	-
3	176	(516)	-	-
4	174	(512)	-	-
5	233	(760)	-	-
6	237	(764)	-	-
7	229	(728)	-	-
8	265	(880)	-	-
9	289	(1000)	-	-
10	303	(1064)	-	-
K_1	250	(712)	-	-
2	282	(860)	-	-
3	317	(1012)	-	-
4	344	(1148)	-	-
5	348	(1152)	-	-

✱ See page 122.

ø These are the values of the initial NaOH-sorption for M^o.

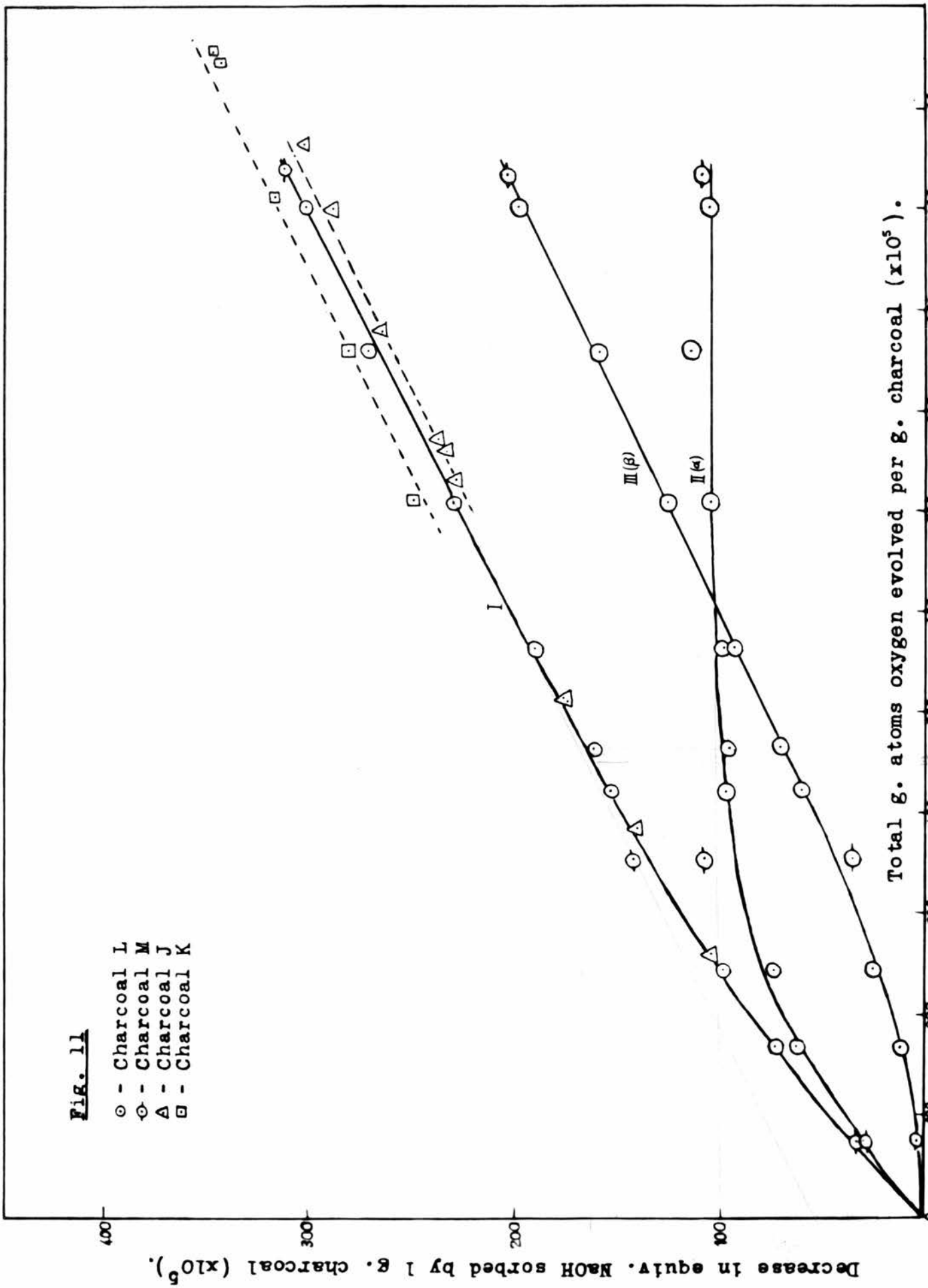
Fig. 11
⊙ - Charcoal L
⊙ - Charcoal M
△ - Charcoal J
⊡ - Charcoal K
Decrease in equiv. NaOH sorbed by 1 g. charcoal (x10⁵).
Total g. atoms oxygen evolved per g. charcoal (x10⁵).
I
II(α)
III(β)
0
100
200
300
400
500
600
700
800
900
1000
1100

In columns 4 and 5 of Table XVIII, the sodium hydroxide sorptions due to α and β (L- and M-series of experiments) are recorded, and the data are plotted in Fig. 11, curves II and III. Curve II shows that the initial rapid loss of sodium hydroxide sorption is entirely due to decomposition of complex α, while curve III indicates that complex β is much more stable and decomposes comparatively slowly. When a total of 600 atoms oxygen have been evolved, curves II and III intersect, at which point decomposition of α is complete, and thereafter the loss of sodium hydroxide sorption is due only to the decomposition of β.

Curve I is simply the sum of curves II and III. The rapid decomposition of α fixes the slope of curve I initially at $\frac{1}{2}$, but as the decomposition of β proceeds its effect is to reduce the gradient. When α has been completely decomposed, oxygen is evolved only by β and the slope of curve I becomes constant at $\frac{1}{4}$.

The position of curve I is affected to a small extent by the value taken for the initial sorption of sodium hydroxide by the oxidised charcoal. The data in column 2 of Table XVIII have been calculated using the mean value of the base-sorptions of charcoals L_1^o and L_2^o which differ by 4%.

It will be noted that the points for charcoals M and J lie close to curve I; also, that J and K give points which lie on lines parallel to the

straight-line portion of curve I. That the scatter is rather greater than in the case of the L-points is to be expected, since the oxygen losses for charcoals J and K are derived from observed losses in weight which are not determined so carefully as in the L- and M-series of experiments.

Variation, from one batch of oxidised charcoal to another, in the relative proportions of the α- and β - complexes would shift the position of the experimental curve, but without alteration in the slope of the straight-line portion. Since the conditions of treatment of the charcoals were not absolutely uniform (both as regards temperature and circulation of the oxygen) it is possible that such variation did occur. Hence the fact that the curve for the K-series lies above curve I is readily explained on the assumption that the ratio of α-complex to β - complex is higher for charcoal K than for L. Similarly, it would appear that the position is reversed in the case of charcoal J, although here the displacement of the curve is much less.

The total sorption of sodium hydroxide by charcoal K^{o} was 359 x 10^{-5} equivalents i.e. considerably greater than by charcoal M^{o} (313 x 10^{-5} equivalents). That K^{o} contained more oxygen than M^{o} (as should be the case if the above interpretation of the results is correct) is shown by the higher loss in weight when degassing is carried far enough to eliminate practically the whole of the sorption of base

(compare Expts. 1 and 2 (M) with K_4 and K_5). It is to be expected that the extra oxygen will be present partly as α- and partly as β - complex. Extrapolation of the K-curve to 359 x 10^{-5} equivalents sodium hydroxide gives 1170 x 10^{-5} g. atoms as the oxygen-content of charcoal K^o. Hence calculation in the manner shown (page 119), gives:

Charcoal K^o

	α complex	β complex	Total
Equiv. NaOH	133	226	359
G. atoms O_2	266	904	1170

Value of ratio:-

O_2 as α-complex/O_2 as β-complex = 266/904 = 0.294, i.e. appreciably higher than for charcoals L^o and M^o (0.265 and 0.267).

Comparison of the decrease in sorption of base with the evolution of carbon dioxide, shows that initially the ratio of moles carbon dioxide to moles sodium hydroxide is unity and that later, when the sorption of base has been reduced by 200 x 10^{-5} equiv., the ratio is again close to unity (at intermediate stages of degassing the ratio is higher). It is therefore tentatively suggested, since initially the α-complex only is decomposing and finally the β-complex alone, that the oxygen atoms composing the α-complex and those forming the acidic part of the β-complex are held in the same way. If this is so, then the additional two oxygen atoms in the β-complex appear to be capable of

stabilising the whole structure. Assuming that the acidic grouping is the same in both complexes, it follows that about 60% of the fixed oxygen is involved in the sorption of base (cf. Strickland-Constable[xiii]).

Weller and Young[xii] found that a sample of oxidised charcoal (TUC-45) having a total oxygen content of 12.7% sorbed 220 x 10^{-5} moles sodium hydroxide. However, charcoal TUC-45 still contained 4.6% oxygen after degassing at 900°, although it then sorbed no alkali, and, therefore only 8.1% oxygen was previously involved in the sorption. According to Fig. 11, this percentage oxygen (equivalent to 500 x 10^{-5} g. atoms per g. charcoal) corresponds to 175 x 10^{-5} moles sodium hydroxide in the case of charcoal L, and nearer 200 x 10^{-5} moles in the case of K. It is evident that the present results are comparable with those of Weller and Young although these workers used charcoal prepared from sawdust, activated with zinc chloride.

The Sorption of Acid

Weller and Young observed that on oxidising their charcoal (CWS N-19) to different extents at 400°, the sorption of sodium hydroxide increased (from zero) with increase in the degree of oxidation, whereas that of hydrochloric acid diminished. Their results, when plotted, show an approximately linear relationship, over the entire range of

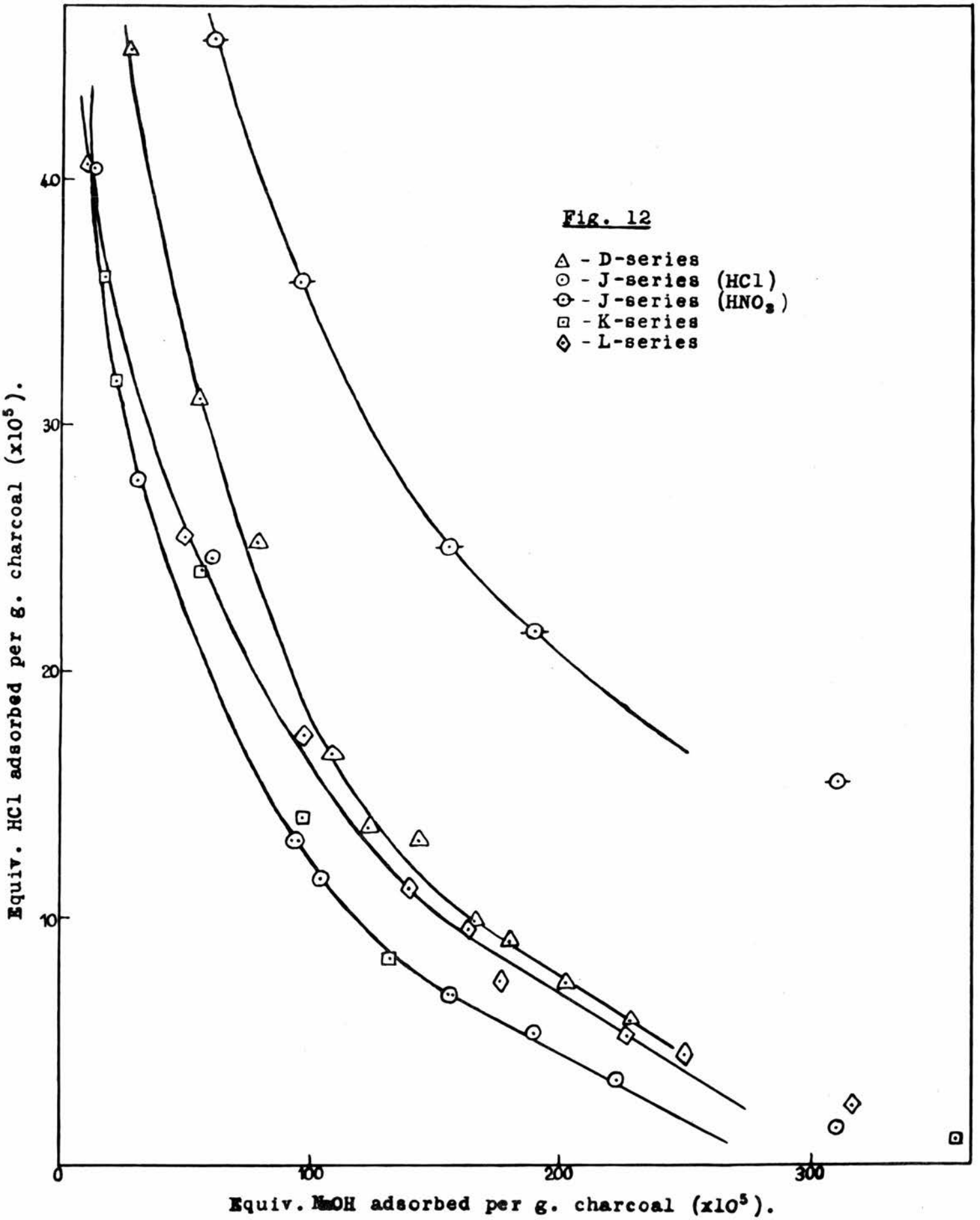
Fig. 12
△ - D-series
⊙ - J-series (HCl)
⊙ - J-series (HNO_3)
⊡ - K-series
◇ - L-series
Equiv. HCl adsorbed per g. charcoal (x10⁵).
Equiv. NaOH adsorbed per g. charcoal (x10⁵).
0
10
20
30
40
100
200
300

measurements, between the amounts of sorbed acid and base.

In the present investigation the degree of oxidation was varied by heating samples of highly oxidised material in a stream of nitrogen (or in vacuo, as in the D-series of experiments) under differing conditions of temperature and time. On plotting the sorptions of sodium hydroxide and hydrochloric acid, the curves shown in Fig. 12 (page 126) are obtained. It will be seen that a linear relationship holds for the early stages of degassing, but that beyond the point at which the sorption of base has been reduced to about 140 x 10^{-5} equiv. the curves bend markedly away from the x-axis. The curves for charcoals D, J and L are very similar, the change in direction occurring at about the same value for the sorption of base, and the K-points lie approximately on the J-curve. Nitric acid shows the same effect, although more strongly sorbed than hydrochloric acid.

Comparison with the data for the sorption of iodine reveals a close parallelism with the sorption of acid. The correspondence is clearly shown in Figs. 13a,b,c,d (pages 128-129), where the sorptions of iodine and hydrochloric acid are plotted, with suitable choice of scales,[1] against the sorption of

[1] Actually the scales are such as to produce coincidence of the points for the iodine and acid sorptions obtained from the first degassing experiment of each series. The data for the initial oxidised charcoal have been ignored since there appears to be a small amount of acid-sorption however large the sorption of base, and also because of the peculiar initial decrease in the sorption of iodine.

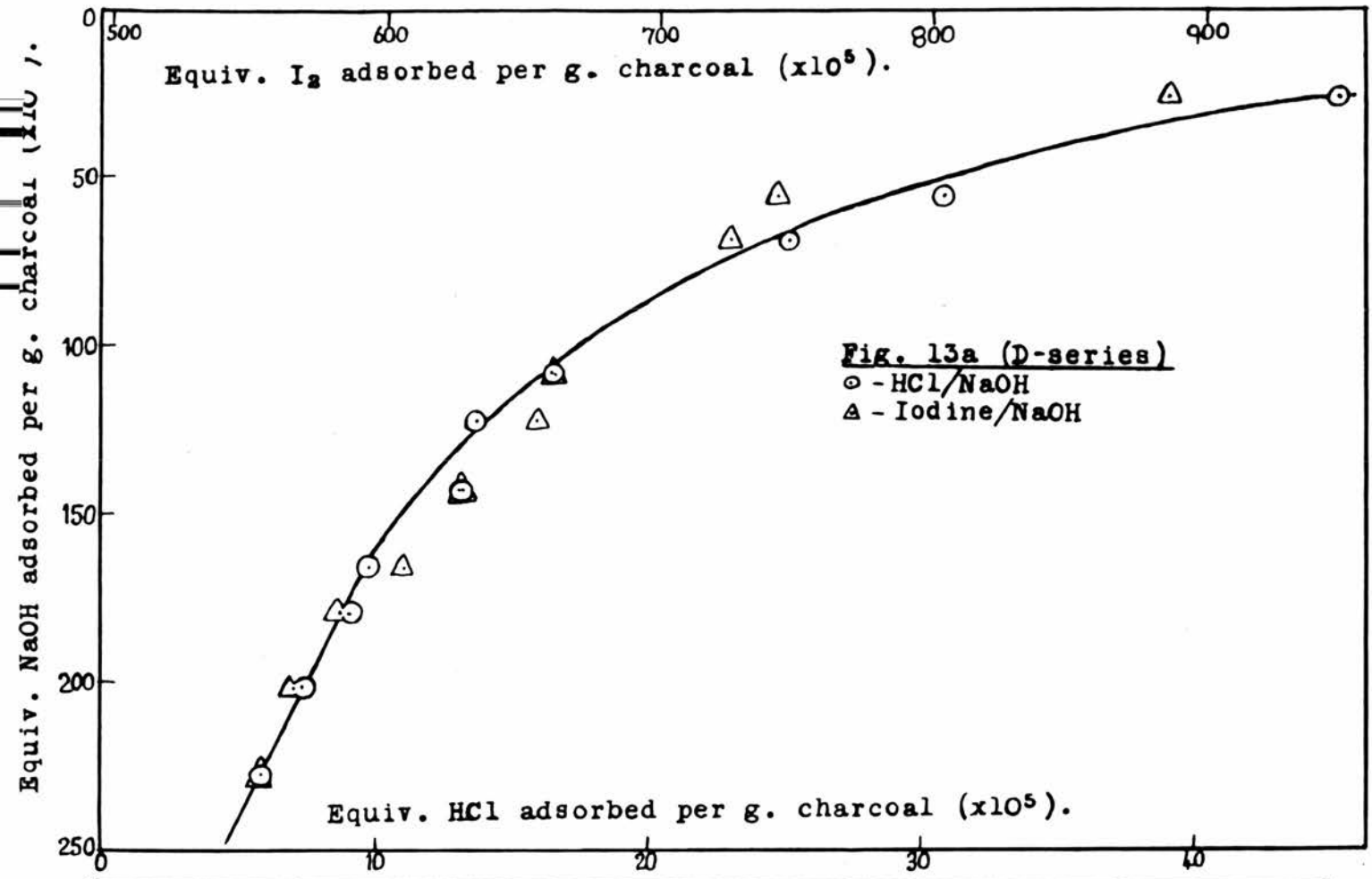

Fig. 13a (D-series)
⊙ - HCl/NaOH
Δ - Iodine/NaOH

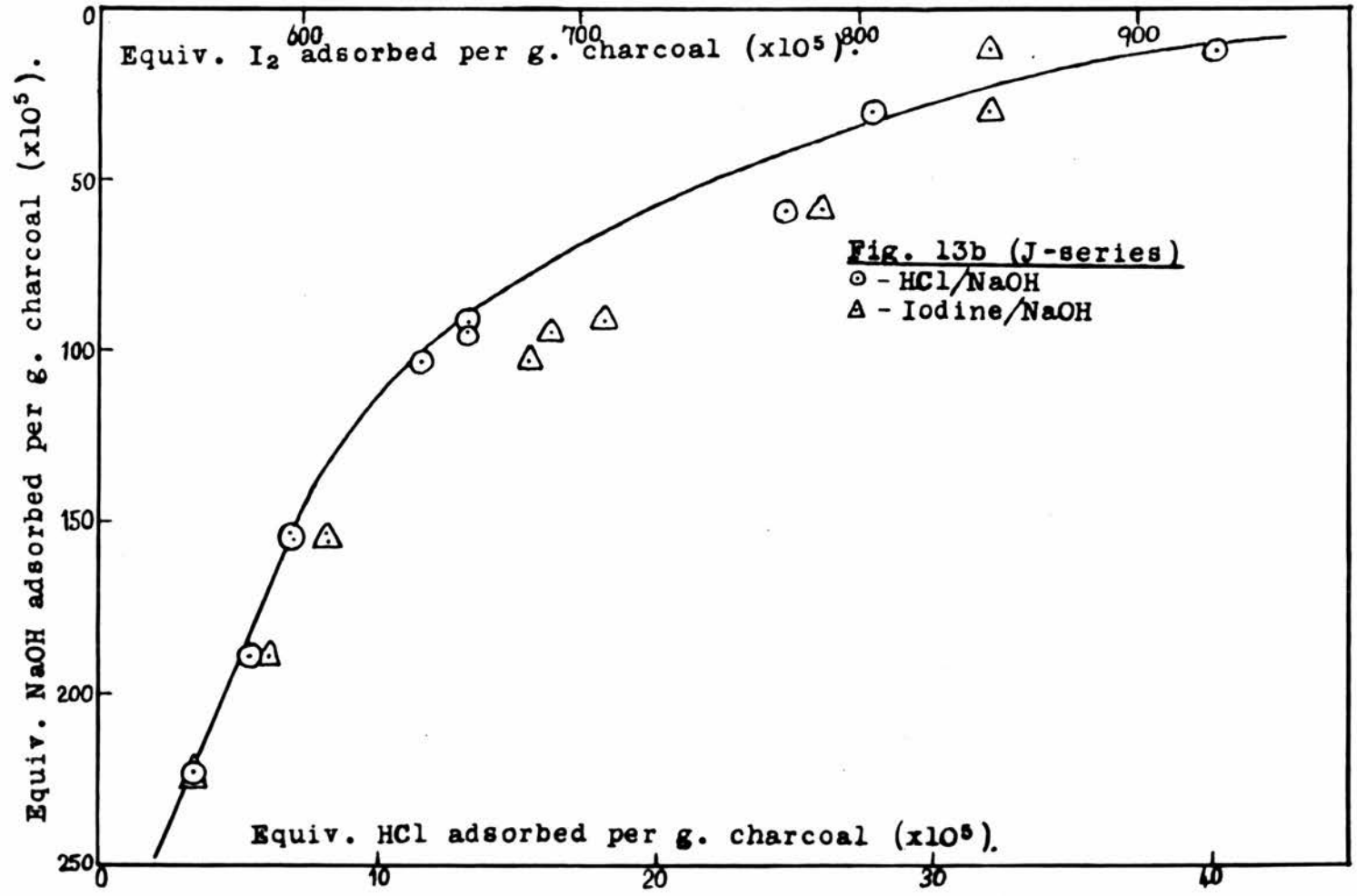

Fig. 13b (J-series)
⊙ - HCl/NaOH
Δ - Iodine/NaOH

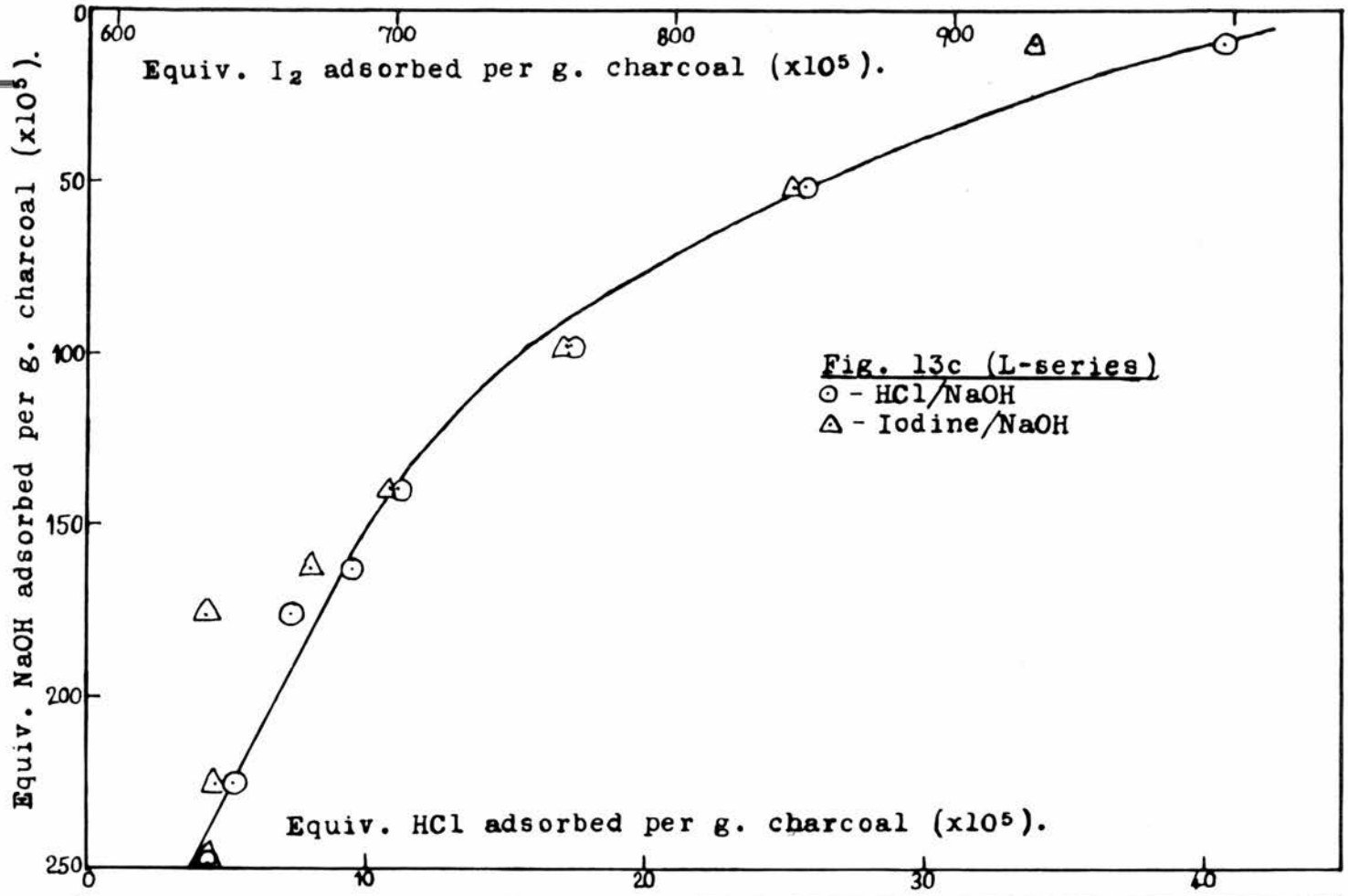

Fig. 13c (L-series)
⊙ - HCl/NaOH
△ - Iodine/NaOH

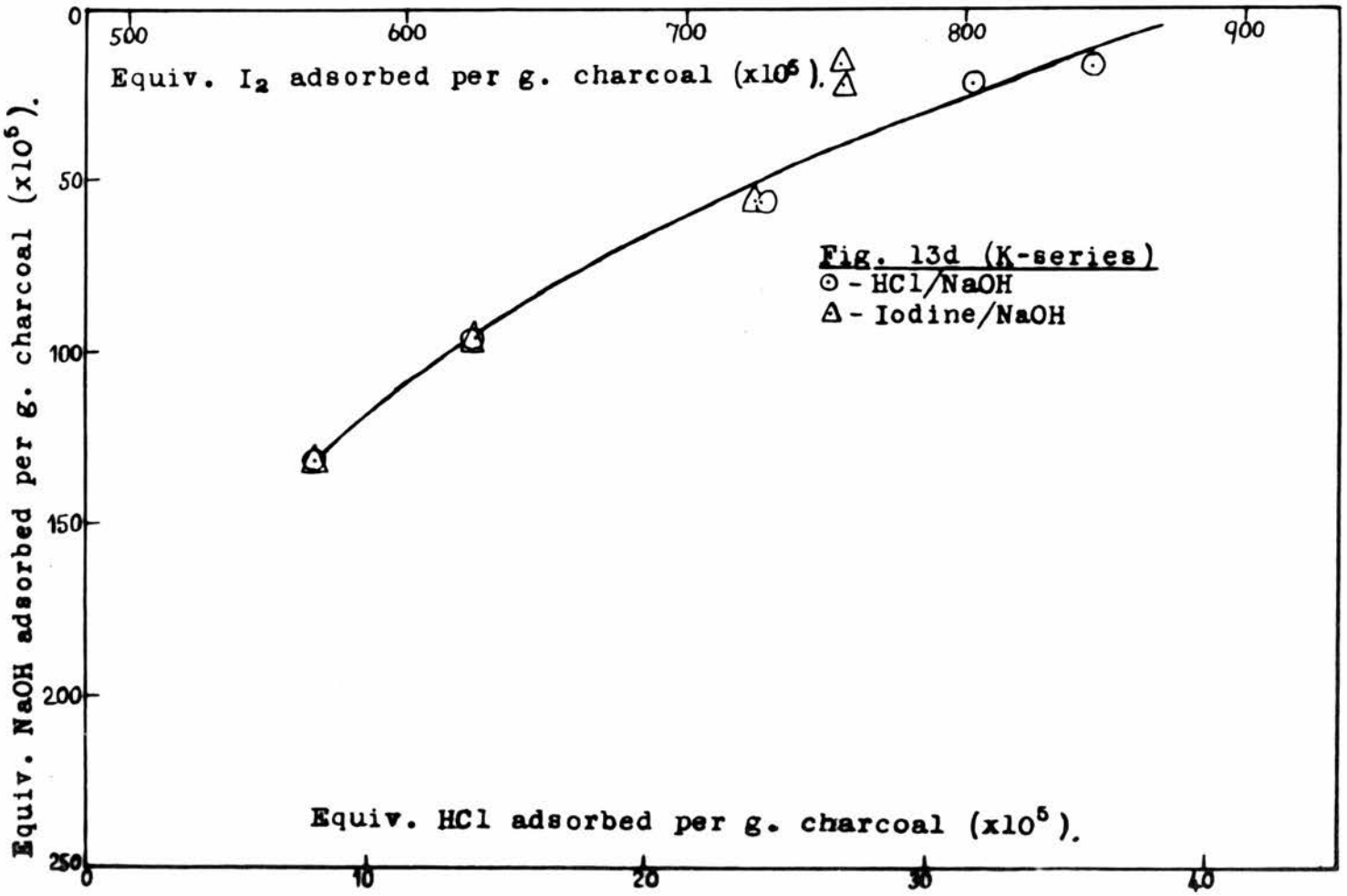

Fig. 13d (K-series)
⊙ - HCl/NaOH
△ - Iodine/NaOH

base. It would appear that the sorption of acid is approximately proportional to the increase in specific surface area of the charcoal produced by the degassing. The sorption of acid is much less than that of iodine, indicating that the former occurs on specific points of the carbon surface. Since it is unlikely that the number of such points per unit area will be constant, the absence of exact correspondence between the sorptions of acid and iodine is not surprising.

The apparent approximate proportionality between increase in sorption of acid and increase in surface area does not favour the hypothesis, first put forward by Schilov, that the sorption of acid is due to interaction with "basic oxide" formed by the decomposition, on heating, of an "acidic oxide" responsible for the sorption of base. On this view one would expect the sorption of acid to be proportional to the decrease in sorption of base, and not to the increase in sorption of iodine. King[iv] also supposes that when charcoal is heated in oxygen, an acidic oxide is preferentially formed at about 400°, and a basic oxide at higher temperatures. However, as shown by Fig. 6 (page 55) and Fig. 12, precisely the same effects are observed when oxidised charcoal is degassed as when evacuated charcoal is treated with oxygen at different temperatures. The sorption of hydrochloric acid obtained by King with charcoal heated in oxygen at

810° differs only to a small extent from that obtained in the present work by heating oxidised charcoal in nitrogen at about the same temperature. If a basic oxide, stable in the region of 800°, does exist, one would expect that a much greater quantity of it would be formed when the charcoal is heated (at this temperature) with a plentiful supply of oxygen, than when oxidised charcoal is simply degassed. Again, the very large difference in magnitude of the sorptions of nitric and hydrochloric acids is clearly anomalous, if it is assumed that the sorption is due to interaction with a basic oxide. Finally, the analytical data (Table XIII, page 96) make it very doubtful if degassing carried out to the extent required for complete elimination of sorption of base, would leave enough oxygen on the charcoal to account for the observed sorption of acid in terms of a basic oxide.

It would seem that the sorption of acid occurs at specific points on the carbon surface, provided these are not occupied by fixed oxygen associated with the sorption of base. Obviously the removal of such oxygen, by degassing, will permit the sorption of acid. However, in addition, the degassing, as already mentioned, apparently produces an increase in the specific surface area of the charcoal, which becomes very marked as the removal of oxygen becomes more difficult (see pages 77 and 114). This increase in surface area evidently

further promotes the sorption of acid. In Weller and Young's experiments, the initial charcoal possessed a large surface area, and relatively smaller changes in surface area were produced by the treatment with oxygen. This would explain the appearance of an approximately linear relationship between the sorptions of acid and base over a much wider range than was observed in this investigation.

In conclusion it may be said that the author's data, as far as they go, support Steenberg's view[1] that the sorption of inorganic acids is in essence the adsorption of hydroxonium ions on carbon atoms in the surface of the charcoal (as opposed to interaction with a surface oxide). However, further investigation is necessary for the elucidation of the phenomenon, particularly as regards the significance of the high pH values exhibited by aqueous suspensions of acid-sorbing charcoals (see King[xvii]).

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[1] As judged from the available abstracts of Steenberg's papers (Chem. Abstracts, 1944, 38, 5446; British Chem. Abstracts, 1947, 242).

SUMMARY

The following have been investigated:-

(1) The influence of treating sugar charcoal with (a) thoroughly dried air at various temperatures, (b) moist air at 370°, (c) moist nitrogen at 430°, on the sorption from aqueous solution of base (sodium hydroxide), acid (hydrochloric acid) and iodine.

(2) The sorption of acid, base and iodine by charcoal, prepared from hexaiodobenzene, treated with air at 430° and oxygen at 425°.

(3) The hydrogen-content of hexaiodobenzene charcoal.

(4) The influence of heating (in nitrogen or in vacuo) base-sorbing (oxidised) sugar charcoal, under various conditions of temperature and time, on (a) the sorption of base, acid (hydrochloric acid and nitric acid) and iodine, (b) the loss in weight, (c) the evolution of water, (d) the evolution of carbon dioxide and carbon monoxide.

(5) The composition of oxidised sugar charcoal.

(6) The isotherms for the sorption by oxidised sugar charcoal of (a) base, (b) iodine.

It has been concluded that:-

(1) Ockrent's hypothesis that the sorption of base by charcoal is due to the presence of high-temperature adsorbed water is untenable.

(2) Sorption of base is due to the presence of chemisorbed oxygen.

(3) Chemisorbed oxygen associated with the sorption

of base appears to consist of two types of complex (termed α and β). Two atoms of oxygen are present in the α-complex, while the β-complex contains four oxygen atoms (there are indications that two of these are grouped as in the α-complex).

(4) At 400° sugar charcoal is capable of fixing very large quantities of oxygen (up to 1 molecule of oxygen to 6 atoms carbon); of this a large proportion is involved in the sorption of base.

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